STUDIES OF DRY ACID DEPOSITION IN THE SOUTH COAST AIR BASIN: INTERMETHOD COMPARISON OF PROCEDURES FOR NITRIC ACID AND AMMONIA

ARB Contract #4-147-32

FINAL REPORT

March 1986

Prepared by

B. R. Appel, Y. Tokiwa, E. L. Kothny, R. Wu and V. Povard

Air & Industrial Hygiene Laboratory
California Department of Health Services
Berkeley, CA 94704

Submitted by

California Public Health Foundation
P.O. Box 520
Berkeley, CA 94701

Prepared for: Research Division
California Air Resources Board
Sacramento, CA 95812

ABSTRACT

A field study was performed at Claremont, CA to evaluate methods for the measurement of atmospheric nitric acid, fine particulate nitrate and gaseous ammonia. The methods employed for nitric acid were the automated, semi-continuous tungstic acid technique (TAT) and the denuder difference method (DDM). Ammonia was measured with the TAT, a filterpack and a manual denuder tube collection method.

The DDM for nitric acid appears to be accurate within about 20%, while the TAT is subject to large variability. Daytime results at Claremont generally show agreement between the TAT and DDM but TAT results are much higher at night. Similarly, TAT ammonia results are uncertain by about a factor of 2. Filter pack ammonia results are consistently too high by, on average, a factor of 1.5, compared to a relatively accurate, manual denuder tube collection technique.

ACKNOWLEDGEMENTS

The tungstic oxide-coated tubes were prepared by Mr. K.M. Hua, visiting professor from Southwest Institute for National Minorities, Chengdu, People's Republic of China. Funding for this work was provided by the California Air Resources Board Research Division.

TABLE OF CONTENTS

TABLE OF CONTENTS
(continued)

FIGURES

TABLES

TABLES
(continued)

I. SUMMARY AND CONCLUSIONS

A field study was performed to evaluate methods for the measurement of gaseous HNO_3, fine particulate NO_3^-, gaseous NH_3 and particulate NH_4^+. The methods employed were (1) a semi-real time technique for HNO_3 and NH_3 utilizing tungstic acid coated denuder tubes (TAT), (2) the denuder difference method (DDM) for HNO_3, fine particle NO_3^- and total fine inorganic NO_3^- (3) a filter pack method for gaseous NH_3 and particulate NH_4^+, and (4) a denuder collection procedure for NH_3 using oxalic acid-coated tubes.

The above samplers were operated at Claremont, CA during the period September 11 through September 19, 1985 in parallel with about 18 other research groups. The emphasis of most of the groups was on HNO_3 measurement, but supplementary measurements were also performed. Comparison of the present results to those from other groups is generally beyond the scope of this contract. However, a comparison of HNO_3 values with those by a spectroscopic method employed by another research groups is included herein.

The DDM yielded HNO_3 results averaging about 30% higher than those by the tunable diode laser (TDL) method. Since partial loss of HNO_3 was probable in the inlet lines of the TDL method, we infer the DDM HNO_3 values to be accurate within about 20%. Compared to the DDM, the TAT results exhibited a pronounced day-night effect; during daylight periods, the TAT and DDM HNO_3 results displayed relatively good agreement. During nighttime hours, when HNO_3 levels were low, the TAT HNO_3 was about 6 times that by the DDM. The cause may relate to collection of NO_x species other than HNO_3. Since NO_2 is not significantly retained on tungstic acid tubes, the results are consistent with at least partial retention of such species as N_2O_5, NO_3 and HONO. These species show enhanced atmospheric concentrations during nighttime hours. This contrasts with our previous results at Riverside, obtained in September 1984 (2), when the TAT was consistently higher by about 30%.

Ammonia results with the TAT were variable in relation to the filter pack (FP) method. The FP/TAT NH_3 ratio of results ranged from 0.6 to 3, increasing with temperature. By comparison to the denuder tube (DT) method, the TAT shows much greater temperature sensitivity than the FP for NH_3 sampling. The present ammonia results with the TAT are considered uncertain by a factor of two. The FP method NH_3 results averaged 50% too high compared to those by the DT method.

II. INTRODUCTION

A. Preceding Studies

As part of preceding ARB-sponsored studies, the Air and Industrial Hygiene Laboratory of the California Department of Health Services (AIHL) evaluated the denuder difference and dual filter (or "filter pack") strategies for atmospheric HNO_3 and NH_3, respectively (1). A recent AIHL study compared these to a semi-continuous tungstic acid technique (TAT) for HNO_3, and, for NH_3, to sampling using oxalic acid-coated denuder tubes (2). The TAT HNO_3 values averaged about 50% higher than those by the denuder difference method (DDM). The cause of this difference was not explainable based on the expected concentrations of interferents and laboratory studies. The possibility that the difference was an experimental artifact could not be refuted.

Earlier intermethod comparisons by this and other laboratories have also revealed substantial differences between HNO_3 procedures in parallel atmospheric sampling (1,3). It is clear, therefore, that the accuracy of most HNO_3 measurement methods remains poorly known. Procedures of proven accuracy are needed to reliably assess atmospheric HNO_3 concentrations. These may be used, for example, in estimating the flux of strong acid being deposited on water and other surfaces.

B. Objectives of the Present Study

The objective of the present study was to perform atmospheric nitric acid and ammonia measurements by several techniques, in parallel with other investigators. The degree of agreement between our methods was assessed. In addition, HNO_3 results were compared to those by a direct, spectroscopic technique provided by another investigator. The methods employed were the TAT for nitric acid and ammonia, the DDM for HNO_3, a filter pack for NH_3 and particulate NH_4^+ as well as a denuder tube collection technique for NH_3. The results obtained are to be analyzed by another ARB contractor to assess the degree of agreement between all investigators.

III. EXPERIMENTAL PLAN

A. Sampling Scheme

Atmospheric sampling for 8 days was done at Claremont, CA during the period September 11 - September 19, 1985. Table 1 lists the samplers employed under the present contract, and Table 2 summarizes the number of integrated samples analyzed in the laboratory. Samplers for the DDM were mounted with inlets facing west, and about 1.5 m above a wooden platform, about 1 meter above a paved surface. Samplers for NH_3 and NH_4^+ faced downward and were located at the same height as the DDM. The TAT was mounted within an air-conditioned mobile laboratory. Outside air was drawn through a 1.5 m by 10 mm I.D. glass manifold employing a squirrel-cage blower. The TAT was connected to this manifold with a line consisting of about 75 cm of 6 mm I.D. glass tubing and 15 cm of FEP Teflon tubing.

B. Description of Samplers

1. Tungstic Acid Technique (TAT)

This method relies on a hydrated tungstic oxide (or tungstic acid)-coated denuder tube to trap and retain HNO_3 and NH_3 (4-6). Figure 1 shows a schematic of the system used. After a 10-minute sampling period at 1 Lpm, a carrier gas, initially He, was introduced from port 2 of a 10-port valve (not shown) while heating the preconcentrator tube. Nitric acid desorbs as NO and/or NO_2 but NH_3 desorbs unchanged. The latter was retained on the transfer tube, a short tube coated with WO_x, downstream of the preconcentrator. The NO_x was converted to NO over a heated gold catalyst and measured with a chemiluminescent NO_x analyzer (TECO Model 14BE). Following emergence of the peak corresponding to HNO_3, the carrier was changed to synthetic air. The transfer tube was then heated and the desorbed NH_3 oxidized to NO over the gold catalyst followed by quantitation as above. The flow rate of the He and synthetic air carrier gas was excess to the sampling rate of the TECO analyzer. The excess was vented through the sample inlet, effectively sealing it

TABLE 1

Sampling Strategy for Intermethod Comparison

Sampler Number	Sampler	Collection Medium	Samples/day	Nominal Sampling Rate, Lpm	Species Measured
1	TAT	tungstic acid (WO_x)	Semi-continuous	1.0	HNO_3, NH_3
2	fine particle NO_3^-	Nylon[a] filter (following MgO-coated denuder)	5[b]	20	fine NO_3^-
3	Total fine NO_3^-	Nylon filter	5	20	fine NO_3^- + HNO_3
4	Diffusion denuder	oxalic acid-glycerine	2	1.5	NH_3 as NH_4^+
5	dual filter NH_3	Teflon[c] prefilter	5	25	NH_4^+ (particle phase)
		2 oxalic acid/quartz filters[d]	5	25	NH_3 (gas phase) as NH_4^+
	chemiluminescent NO_x (Monitor Labs)[e]	-----	Continuous		NO, NO_2
	EG & G Model 911 R.H. and T monitor	-----	Continuous		% R.H., T (°C)
	Dasibi O_3 monitor	-----	Continuous		O_3

a. Nylasorb (47 mm dia.) filters, Gelman Inc., Batch 871.

b. 0800-2400 hr, 4 hour samples. 0000-0600 hr, one 6-hr sample.

c. Two µm pore size Zefluor (47 mm dia.), Gelman Inc.

d. Pallflex 2500 QAO (47 mm dia.) quartz fiber filters, Pall Corp. Glycerine also added.

e. Sampler malfunctioned. No data obtained.

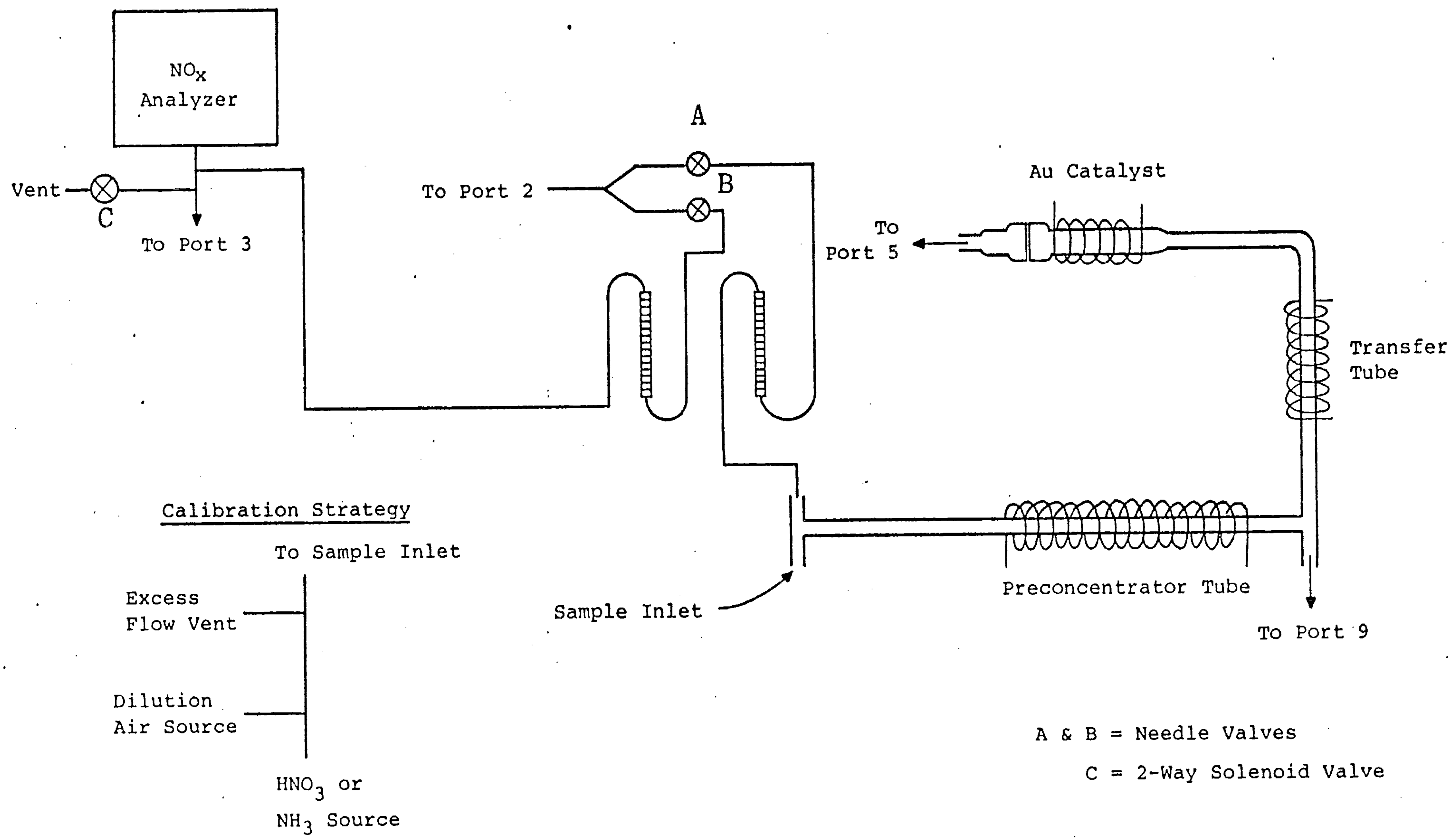
TABLE 2

Filter Samples for Analysis (Number of Determinations[a])

Sampler[b]	Medium	NO_3^-	NH_4^+
2	Nylon	44	
3	Nylon	44	
4	oxalic acid-glycerine		16
5	Teflon		44
6	oxalic acid/ quartz		44
	Totals:	88	104

a. Includes 10% duplicate analyses to assess analytical precision where feasible.

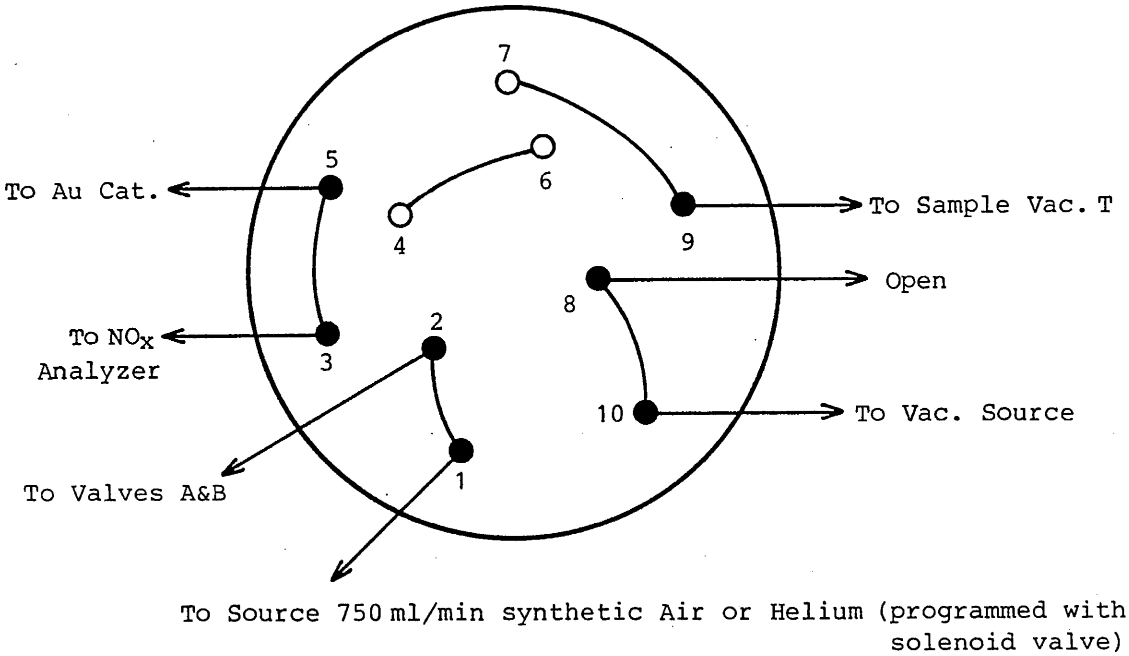
b. See Table 1 for description.



SCHEMATIC OF MODIFIED TUNGSTIC ACID TECHNIQUE

Figure 1A.

ANALYTICAL CYCLE



SAMPLE CYCLE

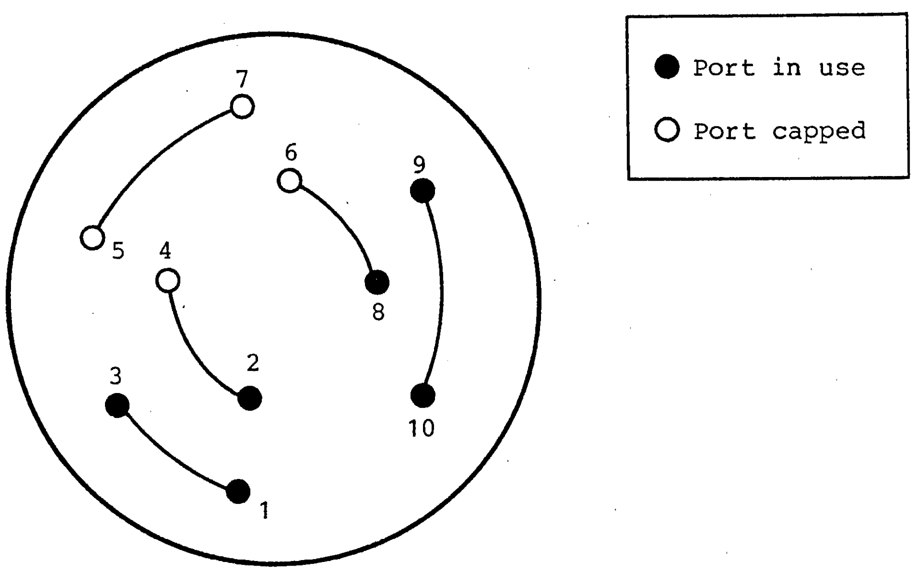


Figure 1B. Schematic of Multiport Valve for Operation of Modified Tungstic Acid Technique.

from intrusion of ambient air during the analytical cycle. The operation of all valves and heaters was controlled by a 10-channel programmable timer (Chrontrol). Mass flow controllers were used for controlling the sampling rate and carrier gas flow. Automated data acquisition and diskette storage was provided by an APPLE IIe microcomputer and an ISAAC System 91A (Dynamic Solutions).

2. Denuder Difference Method

Sampler 2 consisted of a Teflon-lined cyclone, 50% cutpoint 2.2 μm at 28 Lpm (7), a denuder containing 24 tubes, each coated for 30 cm with MgO following initial 10-cm uncoated sections, and a Nuclepore polycarbonate filter holder containing one Nylon filter. Sampler 3 differed from 2 only by the absence of the denuder.

Samplers 2 and 3 were employed in parallel to measure fine particle NO_3^- and fine particle NO_3^- plus HNO_3 respectively. (Sampler 3) - (Sampler 2) NO_3^- results provides HNO_3 measurement by difference. Mass flow controllers on each sampler provided a precision of about 1% at 20 Lpm (8 Lpm of the total flow to each sampler was vented direct to the pump).

3. Ammonia Samplers

Sampler 4 consisted of a 50-cm, 4-mm ID tube coated for 35 cm with an oxalic acid-glycerine mixture following etching with 50% HF solution. The coating was prepared by drawing up into each tube a methanol solution containing 1.5%w oxalic acid and 6.3%w glycerine. Solvent was evaporated by a stream of N_2.

Sampler 5 consisted of a two section, Nuclepore multiple 47-mm filter holder. A Teflon prefilter removed particulate NH_4^+, allowing NH_3 to penetrate to two, oxalic acid-glycerine-impregnated filters, both contained in the same section of the holder. These filters were prepared by spotting each 47 mm Pallflex QAO quartz fiber disc with 0.7 ml of an ethanol solution containing 5.0%w oxalic acid and 5.2%w glycerine. Filter spotting was done in a nitrogen atmosphere, and solvent removed in a stream of N_2. Filters were packaged under N_2 with two discs per Millipore plastic petri dish, sealed, in turn, inside plastic bags.

IV. ANALYTICAL STRATEGY AND QUALITY ASSURANCE

A. Analytical Strategy

Immediately after sampling, all filters were cut into strips and inserted into 15-ml polystyrene screwcap centrifuge tubes, subsequently used for extractions. Teflon filter samples were stored over dry ice; the remainder were stored at ambient temperature within the air-conditioned van. Denuder tubes for NH_3 collection were sealed with Parafilm.

Nylon and NaCl/Whatman 41 filter NO_3^- samples were extracted in 10 ml ion chromatography eluent (0.003 M $NaHCO_3$ - 0.0024 M Na_2CO_3) by one-hour mechanical shaking at room temperature. Oxalic acid/quartz filters for NH_4^+ measurement were extracted as above, but in glass-distilled water. Teflon filter samples for NH_4^+ were also extracted in distilled water. However, these were given an additional one hour agitation in a Fisher RotoRack. Oxalic acid-coated denuder tubes for NH_4^+ measurement were extracted by immersing the downstream end in 5 ml glass-distilled water and repeatedly drawing water up to within 5 cm of the top of the tube (the upper 15 cm were not coated with the acid). Nitrate determinations were made with a Dionex Model 14 ion chromatograph. Ammonium determinations were done with a specific ion electrode.

B. Precision

Precision of wet chemical analyses was assessed by duplicate determination of extracts from eight NO_3^- (on Nylon) and eight NH_4^+ on oxalic acid/quartz fiber filters. The re-analyses were performed about one month following the initial trial, with extracts stored at room temperature in the interim. For NH_4^+ in extracts, the median coefficient of variation (C.V.) was 4.8% (n=8, range 0-22%). For NO_3^-, the median C.V. was 3.1% (n=8, range 0.8-8.1%) for solutions ranging from 1.4 to 12 µg/ml.

C. Accuracy by Field Measurements

Analytical accuracy of nitrate determination was assessed by analysis of Nylon and Teflon filters spiked with known amounts of $NaNO_3$ (Columbia Scientific).

Teflon filters had been sprayed with a water-soluble, polymeric coating to minimize losses in handling. Three filters at each of three NO_3^- levels were extracted, as described above. The results given in Table 3 indicate that with 10 µg samples on Nylon, (ca 1 µg/ml extract concentration), recoveries were too low by about 20%. At higher levels, recoveries from Nylon were about 100%. Results for spiked Teflon filters were more variable; over the range 25-250 µg/filter, recovery of nitrate averaged 96 $\pm$ 9%.

Accuracy of HNO_3 measurement at the sampling site, including both sampling and analysis, was assessed by introducing known dosages of HNO_3 into samplers 2 and 3 used for the DDM, and into the TAT. The sources were permeation tubes supplied and calibrated by A. Weibe. Samples were transported from the source to the sampler through a pre-conditioned 1/8" Teflon line of estimated 20 m length. The separate permeation tubes used for the DDM and TAT samplers were calibrated by collecting bubbler samples immediately following dosing of the DDM or TAT systems. For the DDM, the 1/8" line was inserted into the 8 mm I.D. inlet of the cyclone for each sampler. The flow through the 1/8" line was about 50 ml/min N_2. The balance of the sample was unfiltered ambient air. During the 30 minute dosing of each sampler, done between 0640 and 0740, 9/13/85, an HNO_3 and fine particulate NO_3^- concentration of 8 µg/m^3, each, was estimated based on DDM results for 0000-0600 and 0800-1200 hr on this date. Thus a 30 minute, 20 Lpm sample should include about 5 µg each of atmospheric HNO_3 and particulate NO_3^-.

For the TAT, the 50 ml/min HNO_3 in N_2 stream was diluted with synthetic air to a combined flow $\leq$ 50 ml/min above the 1.0 Lpm sampling rate of the TAT. The diluted sample was attached to the TAT system inlet through a glass T to permit venting of the excess flow.

The results for both systems are given in Table 4. The particulate NO_3^- sampler yielded close to the NO_3^- values expected for atmospheric particulate NO_3^-. However, HNO_3 measured by difference corresponded to only one-fourth of the level expected. The results for total NO_3^-, 12.2 µg, compares to an expected value of 49 µg from the combined atmospheric and permeation tube sources.

TABLE 3

Recovery of Nitrate from Spiked Filters

Filter Type	Code	Mean Observed NO_3^- (μg)[a]	True NO_3^- (μg)	Recovery %
Nylon	100 series	7.1 ± 0.7	9.9 ± 0.1	71.7
	200 series	67 ± 1	69 ± 0.1	97.1
	300 series	194 ± 1	197.7 ± 0.5	98.1
Teflon	400 series	22 ± 0	24.85 ± 0.04	88.5
	500 series	79 ± 0	74.85 ± 0.14	105.5
	600 series	233 ± 3	249 ± 0.6	93.6

a. Results are means ± standard deviation for three filter samples for each series.

TABLE 4

Field Measurement of Accuracy of HNO_3 Measurement by the DDM and TAT

Sampler	HNO_3 Dosage from Perm. Tube (μg)	Observed NO_3^- (μg)	Calculated HNO_3 (μg)	HNO_3 Recovery (%)
Particulate NO_3^-	ca. 39	5.7	6.5	see text
Total NO_3^-	ca. 39	12.2		see text
TAT	0.318		0.250 ± .020	79

Thus observed total NO_3^- is also only one-fourth of that expected. The cause is unknown.* For the TAT, the measured HNO_3 represented a recovery of 79%.

D. Laboratory Evaluation of the Loss of HNO_3 in Teflon-Lined Cyclones and Accuracy of the DDM

To assess loss of HNO_3 in the samplers and the accuracy of the denuder difference method (DDM) for HNO_3 under controlled conditions, HNO_3 from a diffusion tube source was diluted with purified ambient air to provide about 15 $\mu g/m^3$ concentrations (as NO_3^-). This concentration represented close to the midrange of the 4-6 hour average concentrations measured at Claremont. The purification system, Purafil and charcoal beds followed by a glass fiber filter, removed SO_2, strong acids, and particulate matter and sharply reduced NO_2 and NO. The HNO_3 in air was adjusted to 50% R.H. and 20^oC and sampled in parallel with four samplers:

1. A 47-mm Nylon filter (Gelman batch 871) at 20 Lpm.

2. As in 1 preceded by a Teflon-lined cyclone (7) and the same glass manifold as employed at Claremont. The total flow through the cyclone was 28 Lpm of which 20 Lpm was sampled through the Nylon filter. The cyclone was not cleaned from prior use at Claremont (where it had been cleaned after every 48 hr period).

3. Same as 1.

4. Same as 2 but with an MgO denuder between a second cyclone and the Nylon filter. The denuder tubes were the same ones used for the last half of the Claremont study (i.e. their efficiency represents a lower limit to that of a fresh denuder).

*Other participants have reported similarly low recoveries, implying a problem with the HNO_3 source.

The results for three, 2-hour sampling trials are shown in Table 5. HNO_3 concentrations decreased by about 25% between the first and the third trials which contributes to the 10-20% C.V. shown for the mean NO_3^- concentrations by each sampler. Loss of HNO_3 in the cyclone (plus associated glass pipe) can best be assessed by comparing mean total fine NO_3^- results (Sampler 2), 15.2 $\pm$ 1.5 $\mu g/m^3$, against the mean NO_3^- recovered from samplers 1 and 3 for all trials, 15.7 $\pm$ 2.1 $\mu g/m^3$. The results are not significantly different, indicating no measureable loss of HNO_3 in a cyclone still dirty from 48-hr sampling in Claremont. Alternatively, the mean ratio, Sampler 2/Sampler 1 and 3, calculated from individual trials, 0.97 $\pm$ 0.07, can be used to reach the same conclusion.

The accuracy of the DDM (in the absence of potential interferents) may be inferred by comparing the mean results (Total Fine NO_3^- - Fine Particulate NO_3^-), 14.3 $\pm$ 1.5 $\mu g/m^3$, to the mean of samplers 1 and 3, 15.7 $\pm$ 2.1 $\mu g/m^3$. Alternatively, the results may be determined separately by trial to eliminate the influence of the concentration change on the variance. Table 6 indicates, by the latter approach, an accuracy for the DDM of 92 $\pm$ 6%. The principal cause of the apparent 8% negative error is the NO_3^- measured with sampler 4. This NO_3^- represents the sum of HNO_3 penetrating the denuder (estimated to be about 0.5 $\mu g/m^3$ or 3% penetration; employing the Gormley-Kennedy equation and the diffusion coefficient for unhydrated HNO_3), and particulate NO_3^- formed from HNO_3 and NH_3 not removed by the air purification system.

E. Calibration of the TAT

1. HNO_3 Calibration

The output from a Metronics Inc. HNO_3 permeation tube, maintained at 83.3°C in a Metronics Dynacalibrator, was diluted with a stream of filtered ambient air scrubbed through an NaCl/Whatman 41 (NaCl/W41) filter to remove HNO_3. The total flow was adjusted to provide a slight ($\leq$ 50 ml/min) excess relative to the sampling rate of the TAT, 1.0 Lpm. During calibration the glass inlet of the TAT was connected to the diluted HNO_3 source, the excess being vented through a T to a dump line or, briefly, to a rotameter. No correction was made for the < 5% error due to

TABLE 5

Loss of HNO_3 in Cyclone of Samplers for the DDM ($\mu g\ NO_3^-/m^3$)[a]

Trial	Nylon Filter (1)[b]	Total Fine NO_3^- (2)[b]	Nylon Filter (3)[b]	Fine Particulate NO_3^- (4)[b]
1	17.5	16.4	18.9	0.8
2	15.7	15.8	14.7	1.0
3	13.5	13.5	14.1	0.8
Mean:	15.6 ± 2.0	15.2 ± 1.5	15.9 ± 2.6	0.9 ± 0.1

a. All results corrected for a laboratory filter blank, 1.2 ± 0 µg/47 mm filter (n=2).

b. Number in parenthesis is sampler number as discussed in text.

TABLE 6

Laboratory Assessment of the Accuracy of the DDM ($\mu g\ NO_3^-/m^3$)

Trial	Nylon Filter	DDM	DDM/Nylon Filter
1	18.2	15.6	0.857
2	15.2	14.8	0.974
3	13.8	12.7	0.920
		Mean:	0.917 ± 0.059

venting the excess flow during calibration sampling. The ca. 50-cm FEP Teflon line carrying diluted HNO_3 remained equilibrated with HNO_3 at all times.

The emission rate of the HNO_3 source was measured by sampling for 18-24 hour periods with NaCl/W41 filters. The mean emission rate, 89.0 $\pm$ 2.8 ng/min (n=3), compares to a value of 96 $\pm$ 9 ng/min measured 1 year earlier with the same source.

Dosage to the TAT was altered by varying the sampling time between 0 and 3 minutes. The TAT was calibrated daily between 0500 and 0900 hours.

2. Ammonia Calibration

A permeation device, containing dilute NH_4OH (6:1 v/v) in a 2.5-cm length of 0.6 cm I.D. Teflon tubing, was maintained at 40^oC. The NH_3 source was diluted with air scrubbed through an oxalic acid-impregnated filter, with total flow adjusted to a small ($\leq$ 50 ml) excess relative to the TAT sampling rate. The remainder of the calibration strategy is the same as for HNO_3.

The emission rate of the NH_3 source was measured by collection for 18-24 hours on oxalic acid/quartz fiber filters. The mean value was 45.1 $\pm$ 5.0 ng/min (n=3) during the atmospheric sampling.

F. Flow Calibrations

Flow control of the denuder difference method is especially important since HNO_3 is measured by difference, and since NO_3^- levels for the two units can be similar in magnitude. Flow was controlled for each sampler (2 and 3) with Unit mass flow controllers (0-30 Lpm full scale). Samplers 4 and 5, the filter pack and denuder for ammonia, respectively, employed rotameters and valves for flow control. A filter was used ahead of the valve with the denuder to prevent plugging by atmospheric particles. The change in flow rate during a sampling period for samplers 4 and 5 was < 5% in all cases.

Dry test meters at the sampling site were used for checks of the mass flow controllers for the TAT and for samplers 2 through 5. The results obtained with the UCLA dry test meter used for 20-30 Lpm calibration were multiplied by 0.979, to correct for its inaccuracy. Results from the EPA dry test meter used for calibration of samplers 1 and 4 at 1-1.5 Lpm (1 liter per revolution), were uncorrected.

Table 7 lists the intended flow rates and those measured by dry test meters at the sampling site. The latter were used in all data reduction.

G. Field Blanks for Samplers

To assess field blank values, filters (or denuder tubes) were mounted on their appropriate samplers and the units operated on ambient air for 30 seconds. Since two samplers employed nylon filters, a total of six nylon field blanks were obtained, three for each unit. Blank samples were stored and handled in the same manner as atmospheric samples. Field blank results and estimated limits of detection are given in Table 8.

H. Stability of TAT Calibration and Comparison of Data Acquisition Techniques

1. Stability of the TAT Calibration for HNO_3 and NH_3

Table 9 summarizes results for daily calibrations of the TAT. Except for 9/15/85, the system was calibrated with the TECO NO_x analyzer on 0-0.5 ppm full scale. The daily HNO_3 calibration equations are based on peak area measurements while those for NH_3 used peak heights; malfunctions of the data acquisition system hampered NH_3 calibration line determination for each day based on peak areas. Over the period 9/14 - 9/18, there was no substantial change in the TAT response such as would indicate deactivation of the WO_x preconcentrator. Accordingly, for data reduction of 0-0.5 ppm range results, all data points were pooled yielding the equations:

$$\text{PK Area} = 0.0470 + 0.000244\ (\text{ng } HNO_3)$$
$$r = 0.994$$
$$n = 14$$

$$\text{PK Area} = -0.000948 + 0.000426\ (\text{ng } NH_3)$$
$$r = 0.994$$
$$n = 11$$

TABLE 7

On-Site Flow Rate Calibrations

Sampler Number	Description	Intended Flow Rate, Lpm	Observed Flow Rate, Lpm
1	Tungstic Acid Technique	1.0	1.06 ± .05
2	Particulate Nitrate Sampler	20	20.87 ± 0.52
3	Total Nitrate Sampler	20	18.47 ± 0.36
4	Ammonia Filter Pack	25	27.07 ± 0.50
5	Ammonia Denuder Tube	1.5	1.52 ± 0.017

TABLE 8

Field Blank Values and Limits of Detection for Nitrate and Ammonium Ions

Type	Analyte	Field Blank (μg/Sampler)[a]	Limit of Detection, $\mu g/m^3$[b]
Nylon filter	NO_3^-	3.0 $\pm$ 0.3	0.1[c]
Teflon filter	NH_4^+	0.5 $\pm$ 0.1	0.1[d]
Oxalic Acid/quartz filter	NH_4^+	9.7 $\pm$ 1.3[e]	0.4
Oxalic Acid/glass tube	NH_4^+	0.3 $\pm$ 0.1	0.2
NaCl/Whatman 41	NO_3^-	2.6 $\pm$0[f]	Not relevant

a. Mean and standard deviations for five or six field blank samples, except as noted.

b. Based on twice the standard deviation of the field blank, and typical air sampling volume, except as noted.

c. Estimate for HNO_3 as the difference between two filter sampler results.

d. A standard deviation of 0.5 μg each was assumed for the sample and blank filter.

e. Results for two, 47 mm filters combined, as employed in atmospheric sampling.

f. n=3.

TABLE 9

TAT Calibration by Day with the APPLE/ISAAC

Date	TECO Range	Slope	Intercept	r	n
		HNO_3 [a]			
9/14	0.5	0.000308	0.0034	-	2
9/15	1.0	0.000105	-0.00128	0.996	3
9/16	0.5	0.000257	0.00386	0.9987	4
9/17	0.5	0.000254	0.00607		5
9/18	0.5	0.000257	0.00446	0.9974	5
		NH_3 [b]			
9/14	0.5	0.000999	-0.00290	-	2
9/15	1.0	0.000416	0.0135	0.999	4
9/16	0.5	0.000851	0.0349	0.9899	7
9/17	0.5	0.0007855	0.0326	0.9985	6
9/18	0.5	0.000770	0.0262	0.982	5

a. PK Area = a + b (ng HNO_3)

b. PK Height = a + b (ng NH_3)

2. Comparison of Data Acquisition Techniques with the TAT

Nitric acid and NH_3 data from the TAT were monitored with an APPLE IIe/ISAAC System 91 as well as with a Hewlett-Packard Model 3380A recorder-integrator. The APPLE IIe/ISAAC was used to reduce all data. The two systems were compared for one day of HNO_3 sampling. The results, expressed in $\mu g/m^3$, are shown in Figure 2. Over the range of atmospheric HNO_3 concentrations encountered, the H-P results were higher by 1-2 $\mu g/m^3$ compared to those by the APPLE/ISAAC.

I. Comparison of Relative Humidity and Temperature Results with those by a Sling Psychrometer

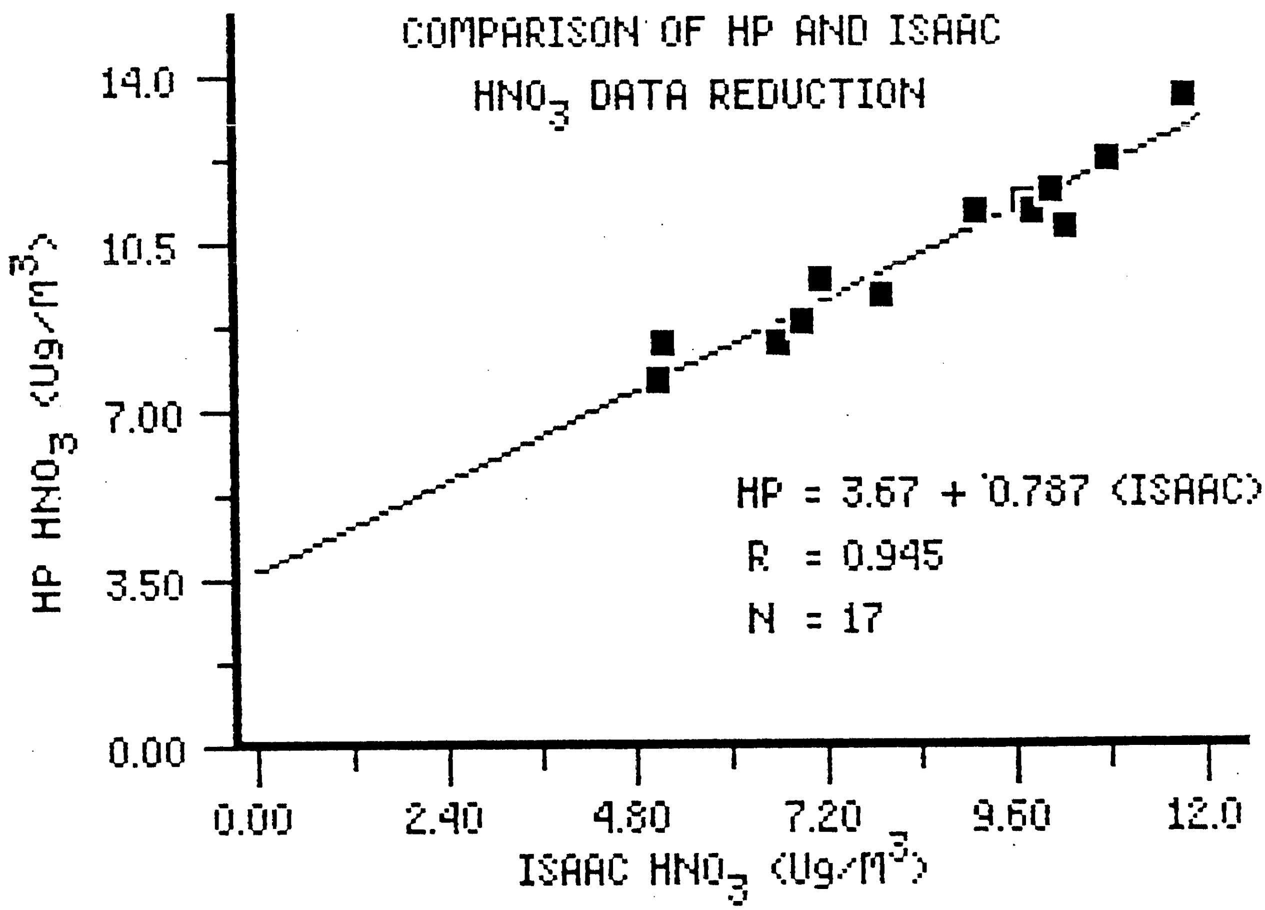
A relative humidity measurement of 32.3% by the EG & G hygrometer compared to a sling psychrometer (PS) value of 44%. Accordingly, our R.H. values in the present study are considered to be too low.

A similar conclusion was reached by comparing EG & G results to those obtained by Southern California Edison in parallel measurements at the site. An EG & G value of 18% compared to 27% obtained by SCE group. The latter had found good agreement with their continuous R.H. monitor and a PS.

The dry temperature measurement of the PS agreed within about 1^oC with the temperature measured with the EG & G unit.

J. Comparison of Different Batches of Nylon Filters

The Nylon filters employed for the present study were identified as Lot No. 871 as supplied by Gelman Sciences, Inc. Other participants in the interlaboratory comparison employed filters from Lot Numbers 4165 and 4015. Substantial differences between lots were observed in the pressure drop across these filters at a given flow rate. Accordingly a brief comparison of filters from each lot was done at Claremont. Several participating groups performed this experiment. This report includes only data from the present investigators.



COMPARISON OF HP AND ISAAC
HNO3 DATA REDUCTION
HP = 3.67 + 0.787 (ISAAC)
R = 0.945
N = 17
14.0
10.5
7.00
3.50
0.00
HP HNO3 (Ug/M3)
0.00
2.40
4.80
7.20
9.60
12.0
ISAAC HNO3 (Ug/M3)

Figure 2

One filter from each of the three lots sampled in parallel for 4 or 10 hour periods. Each was preceded by a 2 µm pore size Teflon filter contained in Nuclepore 47 mm dual filter holders.

Nitrate recovered from the Teflon prefilter has frequently been used to estimate particulate NO_3^-, and the NO_3^- on Nylon after-filter, HNO_3. Table 10 accordingly reports "Apparent Particulate NO_3^-" and "Apparent HNO_3" based on this filter-pack approach. Since open face samplers were used, Teflon filter results approximate total particulate values (i.e., results without particle size segregation).

The results suggest a substantial variation in pressure drop among the three lots. Nevertheless, the recovered NO_3^- from the Nylon filters (i.e., apparent HNO_3) shows little or no difference for the two trials. Apparent particulate NO_3^- values were not significantly different for the three parallel samples.

These results may be compared to those for fine particulate NO_3^- and HNO_3 by the denuder difference method (DDM). For the daytime and nighttime sampling periods, the DDM yielded fine particle NO_3^- values of 12.7 and 7.4 µg/m^3, respectively. Thus relatively high coarse NO_3^- is inferred for the nighttime period. For the same periods, DDM HNO_3 values were 9.1 and 1.8 µg/m^3, respectively. Thus daytime filter-pack HNO_3 values are substantially too high, consistent with prior studies (1).

TABLE 10

Comparison of Nylon Filter Lots in Filterpack Sampling

for Apparent Particulate Nitrate and HNO_3 (Ug/m^3)[A]

Starting Date	Sampling Period	Lot No. (code)	$\triangle P$ (inches Hg)[B]	Apparent Partic. NO_3	Apparent HNO_3[C]
09/16/85	1200-1600	871 (L)	2.5	14.8	16.2
9/16	1200-1600	4015 (O)	0.5	14.7	16.1
9/16	1200-1600	4165 (H)	6.5	14.6	16.1
9/16	2000-0600	871 (L)	2.5	20.1	1.48[D]
9/16	2000-0600	4015 (O)	0.5	19.6	1.49[D]
09/16/85	2000-0600	4165 (H)	6.5	19.5	1.25[D]

[A] Each Nylon filter preceded by a 2 um pore size Zefluor (Teflon) filter.

[B] Sampling rate 15 Lpm with 47 mm filters.

[C] Ug/m^3 as NO_3. A blank correction of 3.0 Ug/filter as measured for batch 871 assumed for all filters.

[D] Final flow rate not measured. Assumed to be 14.7 Lpm, as in prior trial.

V. SUMMARY OF ATMOSPHERIC RESULTS

A. Introduction

This section lists atmospheric results obtained with each sampler. Comparison of results between methods and other data analyses are given in Section VI.

B. Nitric Acid and Ammonia Measured with the Tungstic Acid Technique

One hour average values were obtained by averaging, in general, results from three, 20-minute sampling cycles, each of which included 10 minutes for sampling and 10 minutes for analysis. Tables 11 and 12 list (in $\mu g/m^3$ and $nmoles/m^3$, respectively) such values for HNO_3 and NH_3 for the period 1000 hours, 9/14 until 0600 hours, 9/19/85. Meaningful TAT results were not obtained for the period 0800 hours, 9/11 - 1000 hours, 9/14/85. These data are also displayed graphically in Figures 3-7. Each graph displays HNO_3 and NH_3 values for about a 20-hour period.

C. Fine Particle Nitrate, Total Fine Inorganic Nitrate, and Nitric Acid by the Denuder Difference Method

Tables 13 and 14 list (in $\mu g/m^3$ and $nmoles/m^3$, respectively) values for fine (< 2.2 μm) particle NO_3^-, total fine NO_3^- (i.e., HNO_3 plus fine particle NO_3^-) and HNO_3 by differences for the period 0800 hours, 9/11 until 0600 hours, 9/19/85.

D. Apparent Nitrite Determinations

Ion chromatographic analysis of nylon filter extracts from the DDM samples showed in some cases small NO_2^- peaks, consistent with the retention of HONO or NO_2. Since prior studies (8) showed no evidence of significant NO_2 retention in Nylon filters with realistic NO_2 concentrations, HONO retention may be the cause. The efficiency of HONO retention on single nylon filters has not been established. However, a tube packed tightly with nylon wool has been shown

TABLE 11

SUMMARY OF ONE HOUR AVERAGE NITRIC ACID AND AMMONIA RESULTS BY THE TUNGSTIC ACID TECHNIQUE

DATE	PERIOD (PDT)	HNO_3 (Ug/M^3 as NO_3^-)	NH_3 (Ug/M^3 as NH_4^+)
09/14/85	1000-1100	18.6	2.2
09/14/85	1100-1200	22.3	1.1
09/14/85	1200-1300	25.3	1.0
09/14/85	1300-1400	26.5	1.8
09/14/85	1400-1500	27.0	2.0
09/14/85	1500-1600	27.5	2.7
09/14/85	1600-1700	27.5	3.7
09/14/85	1700-1800	48.6	1.7
09/14/85	1800-1900	35.8	2.0
09/14/85	1900-2000	35.8	2.4
09/14/85	2000-2100	31.5	2.5
09/14/85	2100-2200	26.1	2.9
09/14/85	2200-2300	19.3	5.0
09/14/85	2300-2400	20.1	4.9
09/15/85	0000-0100	22.8	4.7
09/15/85	0100-0200	20.0	4.3
09/15/85	0200-0300	16.4	4.4
09/15/85	0300-0400	14.6	4.2
09/15/85	0400-0500	13.7	4.3
09/15/85	0500-0600	16.8	4.6
09/15/85	0600-0700	N.D.[A]	N.D.
09/15/85	0700-0800	N.D.	N.D.
09/15/85	0800-0900	N.D.	N.D.
09/15/85	0900-1000	21.3	3.2
09/15/85	1000-1100	24.7	3.4
09/15/85	1100-1200	25.0	2.1
09/15/85	1200-1300	23.1	N.D.
09/15/85	1300-1400	26.7	3.2
09/15/85	1400-1500	22.3	2.7
09/15/85	1500-1600	17.7	2[B]
09/15/85	1600-1700	15.5	2.0
09/15/85	1700-1800	20.6	2.5
09/15/85	1800-1900	16.7	2.6
09/15/85	1900-2000	11.8	4.0
09/15/85	2000-2100	11.0	4.7
09/15/85	2100-2200	7.1	4.9
09/15/85	2200-2300	6.7	5.7
09/15/85	2300-2400	5.7	5.6

TABLE 11 (Contd.)

DATE	PERIOD (PDT)	HNO_3 (Ug/M^3 as NO_3^-)	NH_3 (Ug/M^3 as NH_4^+)
09/16/85	0000-0100	4.6	5.3
09/16/85	0100-0200	6.2	4.7
09/16/85	0200-0300	7.0	4.9
09/16/85	0300-0400	6.3	4.8
09/16/85	0400-0500	5.2	4.7
09/16/85	0500-0600	5.1	4.9
09/16/85	0600-0700	N.D.	N.D.
09/16/85	0700-0800	N.D.	N.D.
09/16/85	0800-0900	N.D.	N.D.
09/16/85	0900-1000	N.D.	N.D.
09/16/85	1000-1100	5.3	8.5
09/16/85	1100-1200	6.4	14.5
09/16/85	1200-1300	7.2	12.9
09/16/85	1300-1400	6.0	5.1
09/16/85	1400-1500	7.4	3.1
09/16/85	1500-1600	9.9	3.0
09/16/85	1600-1700	5.8	1.9
09/16/85	1700-1800	8.0	2.1
09/16/85	1800-1900	6.7	2.9
09/16/85	1900-2000	5.0	3.0
09/16/85	2000-2100	2.6	2.3
09/16/85	2100-2200	3.3	3.5
09/16/85	2200-2300	3.6	3.1
09/16/85	2300-2400	3.3	3.0
09/17/85	0000-0100	3.7	3.1
09/17/85	0100-0200	3.6	3.6
09/17/85	0200-0300	4.0	2.6
09/17/85	0300-0400	N.D.	N.D.
09/17/85	0400-0500	3.8	2.0
09/17/85	0500-0600	N.D.	N.D.
09/17/85	0600-0700	N.D.	N.D.
09/17/85	0700-0800	N.D.	N.D.
09/17/85	0800-0900	4.8	4.6
09/17/85	0900-1000	2.7	7.3
09/17/85	1000-1100	3.1	18.1
09/17/85	1100-1200	4.6	27.0
09/17/85	1200-1300	8.2	19.1
09/17/85	1300-1400	6.2	7.7
09/17/85	1400-1500	9.5	4.4
09/17/85	1500-1600	6.1	2.4
09/17/85	1600-1700	N.D.	N.D.
09/17/85	1700-1800	11.2	5.7
09/17/85	1800-1900	9.9	3.8
09/17/85	1900-2000	10.5	2.9
09/17/85	2000-2100	7.7	2.8
09/17/85	2100-2200	6.8	3.4
09/17/85	2200-2300	5.8	3.2
09/17/85	2300-2400	5.3	3.0

TABLE 11 (Contd.)

DATE	PERIOD (PDT)	HNO_3 (Ug/M^3 as NO_3^-)	NH_3 (Ug/M^3 as NH_4^+)
09/18/85	0000-0100	5.7	2.8
09/18/85	0100-0200	6.1	3.4
09/18/85	0200-0300	5.4	3.1
09/18/85	0300-0400	5.9	2.9
09/18/85	0400-0500	6.3	3.1
09/18/85	0500-0600	N.D.	N.D.
09/18/85	0600-0700	N.D.	N.D.
09/18/85	0700-0800	N.D.	N.D.
09/18/85	0800-0900	5.1	3.7
09/18/85	0900-1000	5.2	3.2
09/18/85	1000-1100	6.6	3.9
09/18/85	1100-1200	6.9	2.9
09/18/85	1200-1300	8.1	2.5
09/18/85	1300-1400	7.5	3.7
09/18/85	1400-1500	6.8	2.1
09/18/85	1500-1600	7.2	1.6
09/18/85	1600-1700	8.0	0.5b
09/18/85	1700-1800	10.8	2.4
09/18/85	1800-1900	10.7[c]	N.D.
09/18/85	1900-2000	10.5[c]	N.D.
09/18/85	2000-2100	10.8	3.4
09/18/85	2100-2200	9.7	3.6
09/18/85	2200-2300	10.8	3.2
09/18/85	2300-2400	9.9	2.7
09/19/85	0000-0100	9.8	2.3
09/19/85	0100-0200	9.1	2.7
09/19/85	0200-0300	10.3	2.5
09/19/85	0300-0400	10.8	2.1
09/19/85	0400-0500	10.1	2.3
09/19/85	0500-0600	11.8	1.7

[A] No data.
[B] Estimated Value
[C] Based on Hewlett-Packard integrator data corrected for bias relative to Apple-ISAAC.

TABLE 12

SUMMARY OF ONE HOUR AVERAGE NITRIC ACID AND AMMONIA RESULTS BY THE TUNGSTIC ACID TECHNIQUE

DATE	PERIOD (PDT)	HNO_3 (nMol/M^3)	NH_3 (nMol/M^3)
09/14/85	1000-1100	300.0	122.2
09/14/85	1100-1200	359.7	61.1
09/14/85	1200-1300	408.1	55.6
09/14/85	1300-1400	427.4	100.0
09/14/85	1400-1500	435.5	111.1
09/14/85	1500-1600	443.5	150.0
09/14/85	1600-1700	443.5	205.6
09/14/85	1700-1800	783.9	94.4
09/14/85	1800-1900	577.4	111.1
09/14/85	1900-2000	577.4	133.3
09/14/85	2000-2100	508.1	138.9
09/14/85	2100-2200	421.0	161.1
09/14/85	2200-2300	311.3	277.8
09/14/85	2300-2400	324.2	272.2
09/15/85	0000-0100	367.7	261.1
09/15/85	0100-0200	322.6	238.9
09/15/85	0200-0300	264.5	244.4
09/15/85	0300-0400	235.5	233.3
09/15/85	0400-0500	221.0	238.9
09/15/85	0500-0600	271.0	255.6
09/15/85	0600-0700	N.D.[A]	N.D.
09/15/85	0700-0800	N.D.	N.D.
09/15/85	0800-0900	N.D.	N.D.
09/15/85	0900-1000	343.5	177.8
09/15/85	1000-1100	398.4	188.9
09/15/85	1100-1200	403.2	116.7
09/15/85	1200-1300	372.6	N.D.
09/15/85	1300-1400	430.6	177.8
09/15/85	1400-1500	359.7	150.0
09/15/85	1500-1600	285.5	111.1[B]
09/15/85	1600-1700	250.0	111.1
09/15/85	1700-1800	332.3	138.9
09/15/85	1800-1900	269.4	144.4
09/15/85	1900-2000	190.3	222.2
09/15/85	2000-2100	177.4	261.1
09/15/85	2100-2200	114.5	272.2
09/15/85	2200-2300	108.1	316.7
09/15/85	2300-2400	91.9	311.1

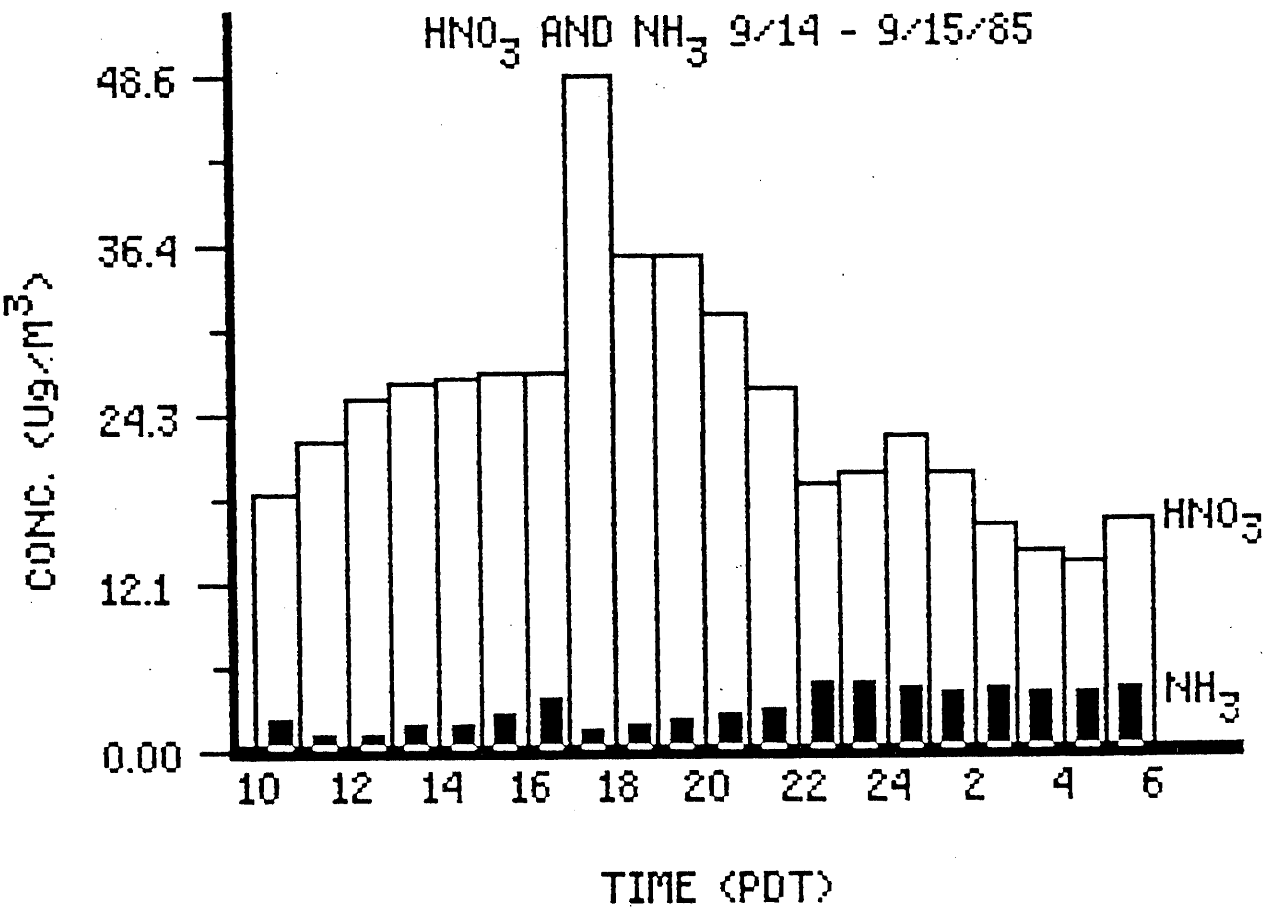
TABLE 12 (Contd.)

DATE	PERIOD (PDT)	HNO_3 (nMol/M^3)	NH_3 (nMol/M^3)
09/16/85	0000-0100	74.2	294.4
09/16/85	0100-0200	100.0	261.1
09/16/85	0200-0300	112.9	272.2
09/16/85	0300-0400	101.6	266.7
09/16/85	0400-0500	83.9	261.1
09/16/85	0500-0600	82.3	272.2
09/16/85	0600-0700	N.D.	N.D.
09/16/85	0700-0800	N.D.	N.D.
09/16/85	0800-0900	N.D.	N.D.
09/16/85	0900-1000	N.D.	N.D.
09/16/85	1000-1100	85.5	472.2
09/16/85	1100-1200	103.2	805.6
09/16/85	1200-1300	116.1	716.7
09/16/85	1300-1400	96.8	283.3
09/16/85	1400-1500	119.4	172.2
09/16/85	1500-1600	159.7	166.7
09/16/85	1600-1700	93.5	105.6
09/16/85	1700-1800	129.0	116.7
09/16/85	1800-1900	108.1	161.1
09/16/85	1900-2000	80.6	166.7
09/16/85	2000-2100	41.9	127.8
09/16/85	2100-2200	53.2	194.4
09/16/85	2200-2300	58.1	172.2
09/16/85	2300-2400	53.2	166.7
09/17/85	0000-0100	59.7	172.2
09/17/85	0100-0200	58.1	200.0
09/17/85	0200-0300	64.5	144.4
09/17/85	0300-0400	N.D.	N.D.
09/17/85	0400-0500	61.3	111.1
09/17/85	0500-0600	N.D.	N.D.
09/17/85	0600-0700	N.D.	N.D.
09/17/85	0700-0800	N.D.	N.D.
09/17/85	0800-0900	77.4	255.6
09/17/85	0900-1000	43.5	405.6
09/17/85	1000-1100	50.0	1005.6
09/17/85	1100-1200	74.2	1500.0
09/17/85	1200-1300	132.3	1061.1
09/17/85	1300-1400	100.0	427.8
09/17/85	1400-1500	153.2	244.4
09/17/85	1500-1600	98.4	133.3
09/17/85	1600-1700	N.D.	N.D.
09/17/85	1700-1800	180.6	316.7
09/17/85	1800-1900	159.7	211.1
09/17/85	1900-2000	169.4	161.1
09/17/85	2000-2100	124.2	155.6
09/17/85	2100-2200	109.7	188.9
09/17/85	2200-2300	93.5	177.8
09/17/85	2300-2400	85.5	166.7

TABLE 12 (Contd.)

DATE	PERIOD (PDT)	HNO_3 (nMol/M³)	NH_3 (nMol/M³)
09/18/85	0000-0100	91.9	155.6
09/18/85	0100-0200	98.4	188.9
09/18/85	0200-0300	87.1	172.2
09/18/85	0300-0400	95.2	161.1
09/18/85	0400-0500	101.6	172.2
09/18/85	0500-0600	N.D.	N.D.
09/18/85	0600-0700	N.D.	N.D.
09/18/85	0700-0800	N.D.	N.D.
09/18/85	0800-0900	82.3	205.6
09/18/85	0900-1000	83.9	177.8
09/18/85	1000-1100	106.5	216.7
09/18/85	1100-1200	111.3	161.1
09/18/85	1200-1300	130.6	138.9
09/18/85	1300-1400	121.0	205.6
09/18/85	1400-1500	109.7	116.7
09/18/85	1500-1600	116.1	88.9
09/18/85	1600-1700	129.0	27.7b
09/18/85	1700-1800	174.2	133.3
09/18/85	1800-1900	172.6[c]	N.D.
09/18/85	1900-2000	169.4[c]	N.D.
09/18/85	2000-2100	174.2	188.9
09/18/85	2100-2200	156.5	200.0
09/18/85	2200-2300	174.2	177.8
09/18/85	2300-2400	159.7	150.0
09/19/85	0000-0100	158.1	127.8
09/19/85	0100-0200	146.8	150.0
09/19/85	0200-0300	166.1	138.9
09/19/85	0300-0400	174.2	116.7
09/19/85	0400-0500	162.9	127.8
09/19/85	0500-0600	190.3	94.4

[a] Estimated Value.
[b] No data.
[c] Based on Hewlett - Packard integrator data corrected for bias relative to Apple/Isaac.



HNO3 AND NH3 9/14 - 9/15/85
48.6
36.4
24.3
12.1
0.00
CONC. (Ug/M3)
10 12 14 16 18 20 22 24 2 4 6
TIME (PDT)
HNO3
NH3

Figure 3

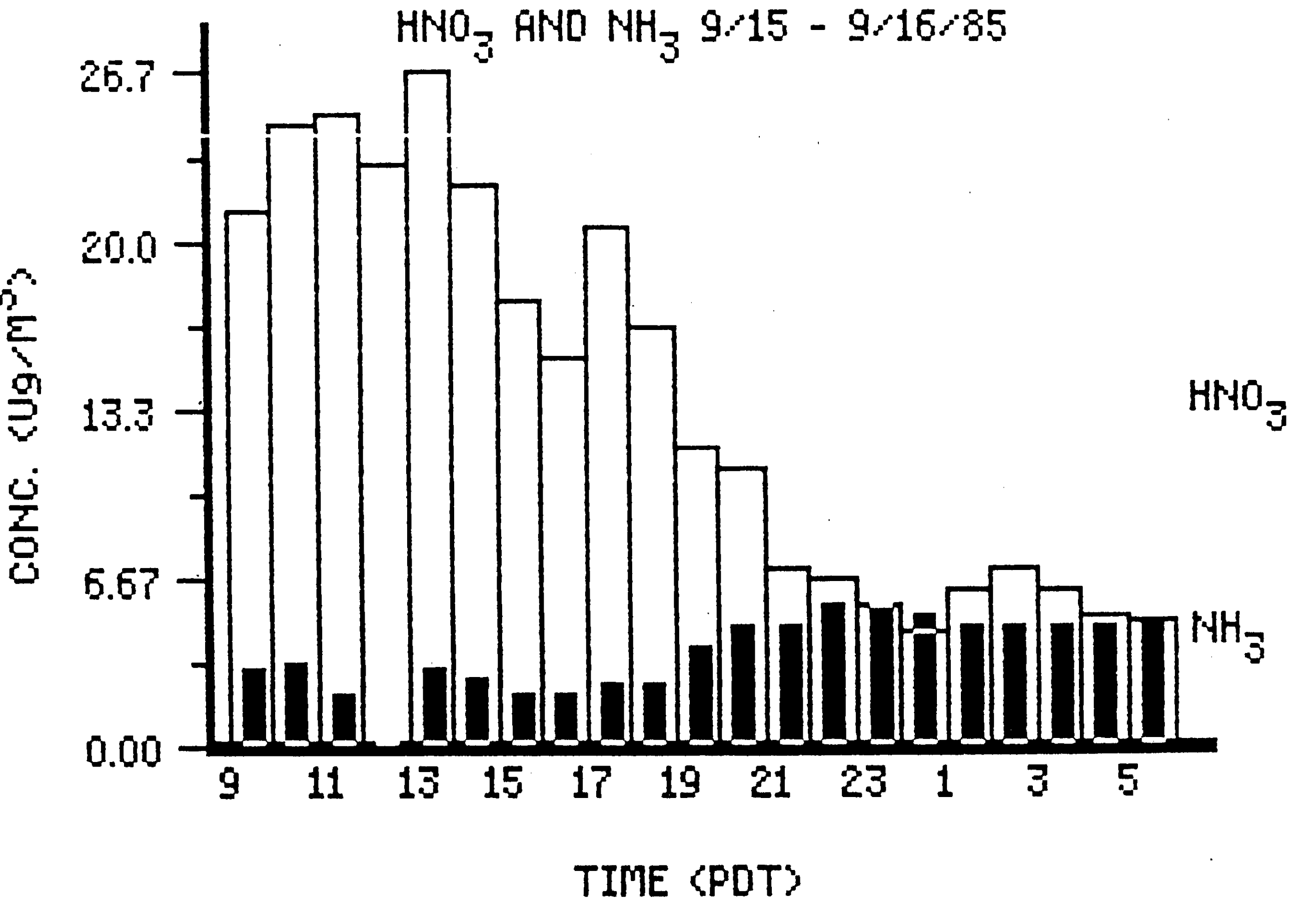
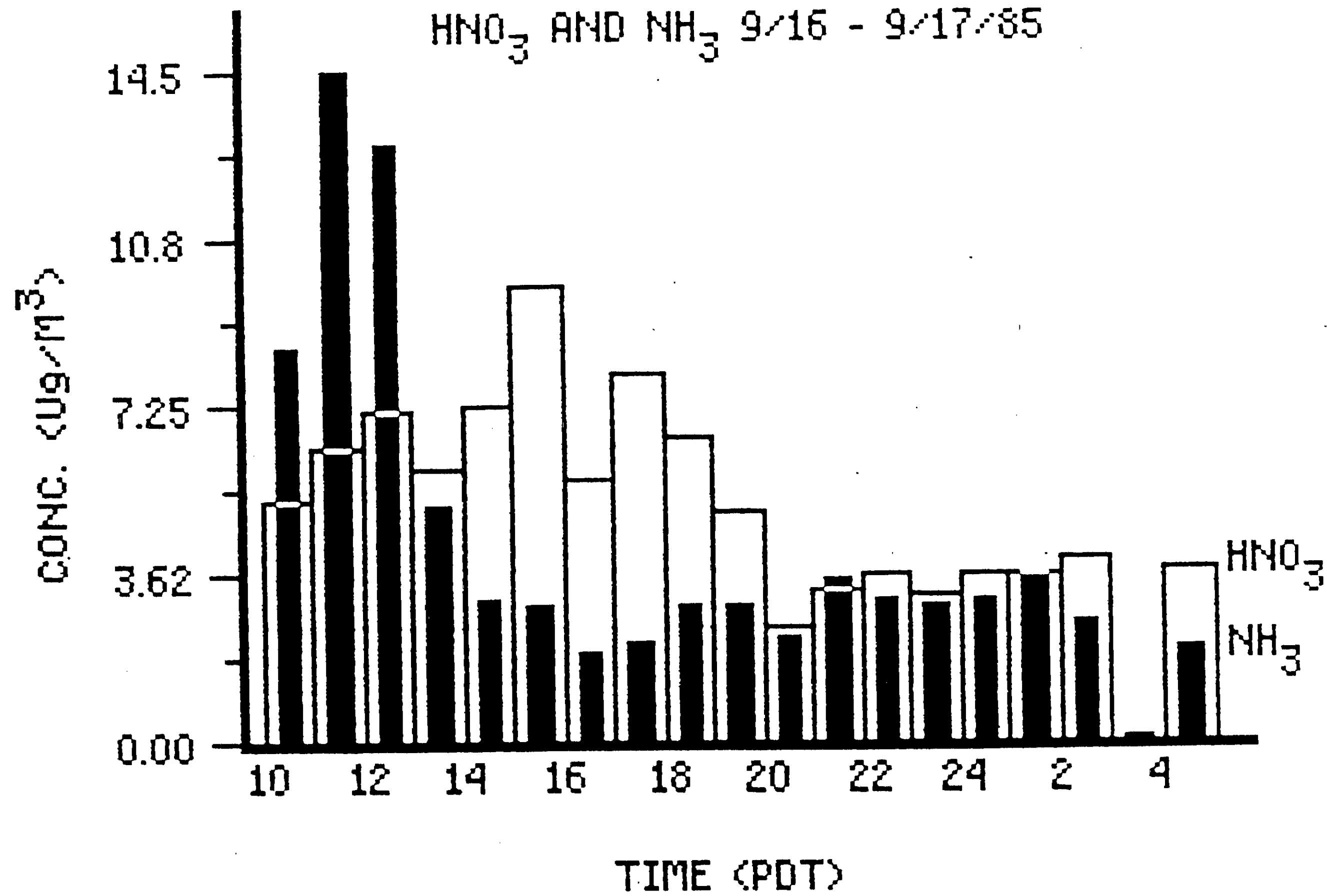
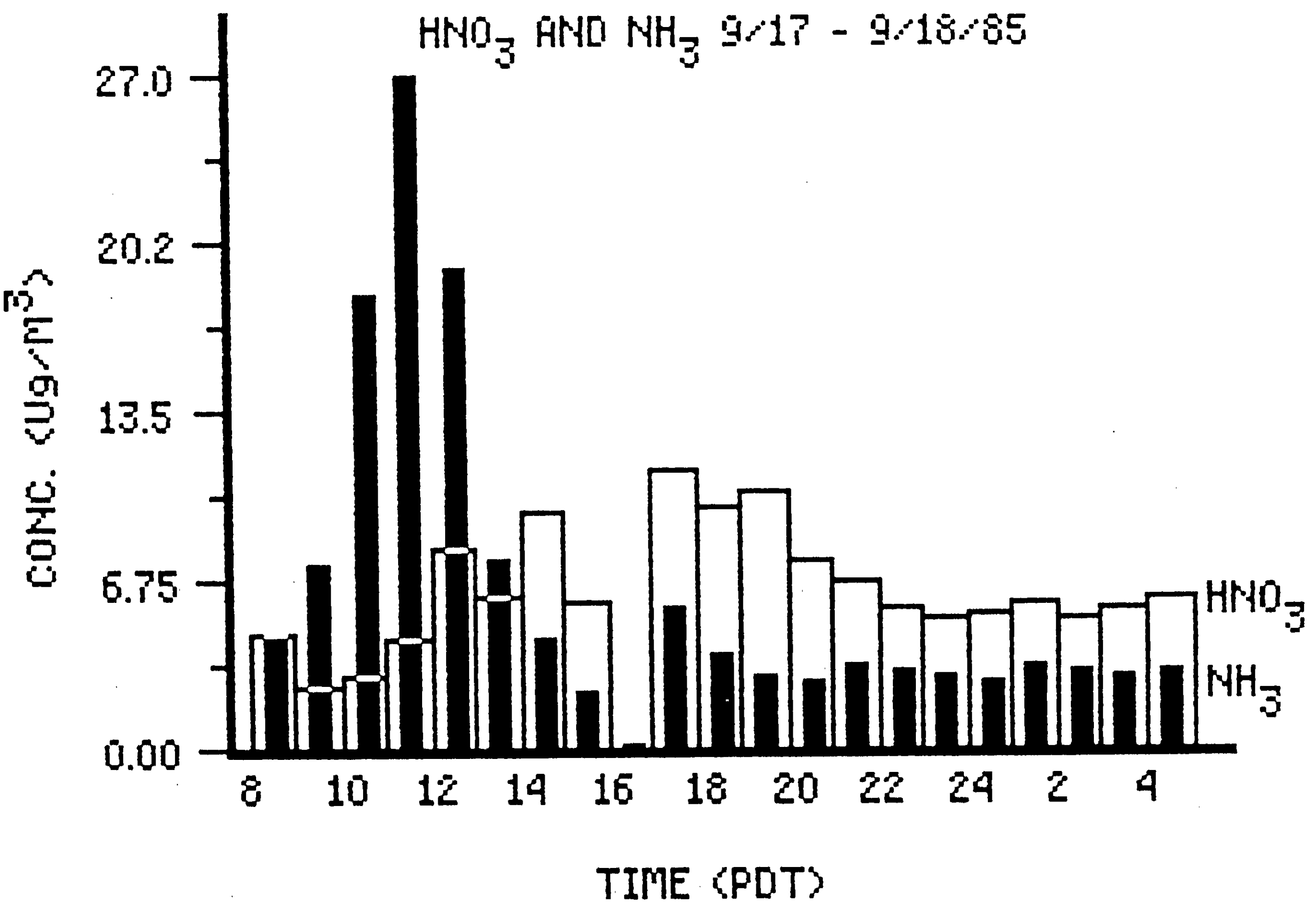

HNO3 AND NH3 9/15 - 9/16/85
26.7
20.0
13.3
6.67
0.00
CONC. (Ug/M3)
HNO3
NH3
9
11
13
15
17
19
21
23
1
3
5
TIME (PDT)

Figure 4



HNO3 AND NH3 9/16 - 9/17/85
14.5
10.8
7.25
3.62
0.00
CONC. (Ug/M3)
10
12
14
16
18
20
22
24
2
4
TIME (PDT)
HNO3
NH3

Figure 5



HNO3 AND NH3 9/17 - 9/18/85
27.0
20.2
13.5
6.75
0.00
CONC. (Ug/M3)
8
10
12
14
16
18
20
22
24
2
4
TIME (PDT)
HNO3
NH3

Figure 6

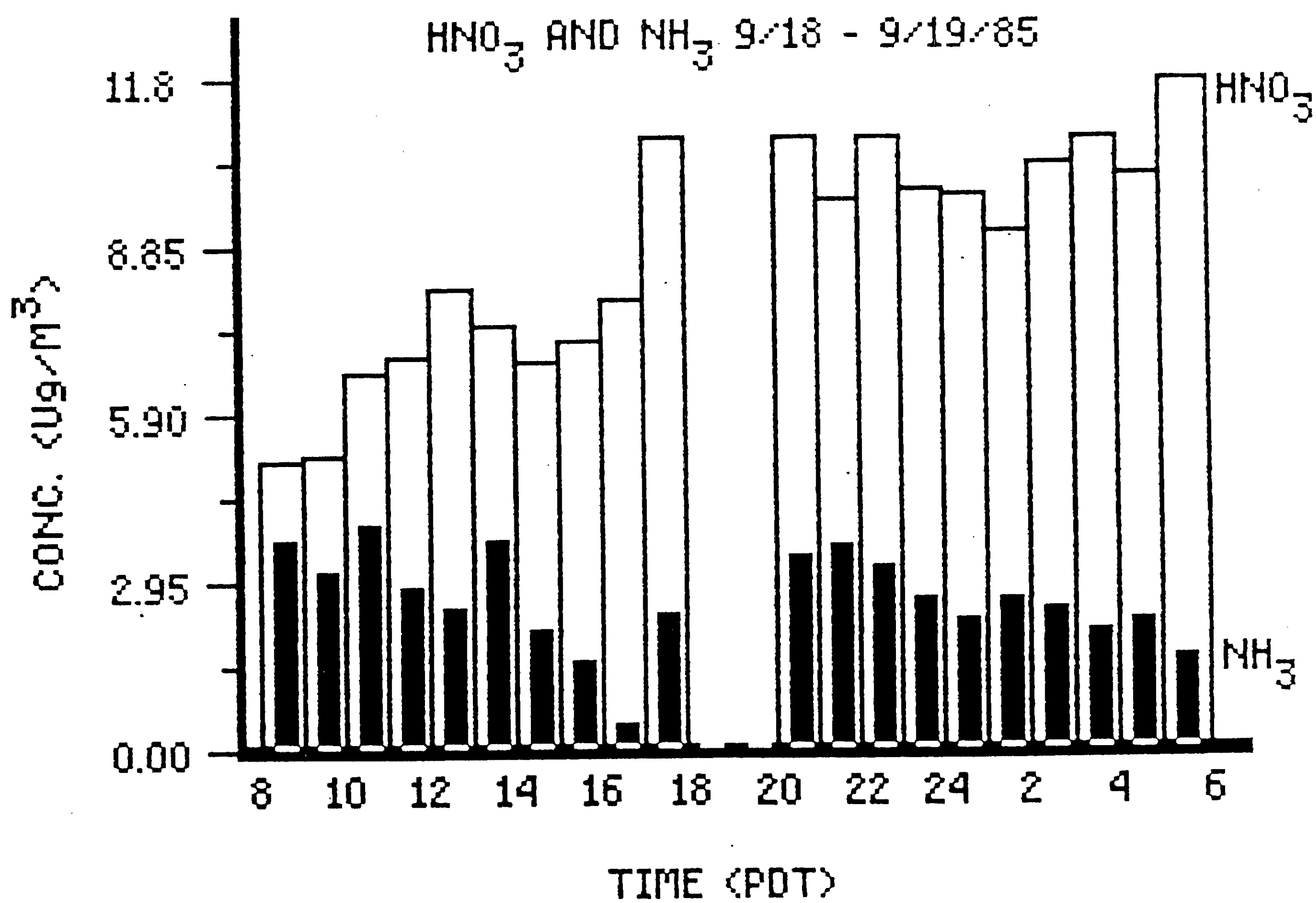

HNO3 AND NH3 9/18 - 9/19/85
11.8
8.85
5.90
2.95
0.00
CONC. <Ug/M3>
HNO3
NH3
8 10 12 14 16 18 20 22 24 2 4 6
TIME <PDT>

Figure 7

TABLE 13

LISTING OF DENUDER DIFFERENCE METHOD RESULTS (Ug/M^3)

DATE	PERIOD (PDT)	TOTAL FINE NO_3^-	FINE PARTIC. NO_3^-	HNO_3 (AS NO_3^-)
09/11/85	0800-1200	2.63	1.61	1.0
09/11/85	1200-1600	7.66	2.32	5.3
09/11/85	1600-2000	5.18	1.79	3.4
09/11/85	2000-2400	1.82	0.65	1.2
09/12/85	0000-0600	2.89	1.86	1.0
09/12/85	0800-1200	14.21	7.26	7.0
09/12/85	1200-1600	20.75	12.19	8.6
09/12/85	1600-2000	37.27	14.67	22.6
09/12/85	2000-2400	17.05	8.83	8.2
09/13/85	0000-0600	10.56	7.15	3.4
09/13/85	0800-1200	23.76	---a	---a
09/13/85	1200-1600	37.15	9.91	27.2
09/13/85	1600-2000	39.73	8.98	30.8
09/13/85	2000-2400	14.77	4.62	10.2
09/14/85	0000-0600	16.37	9.42	7.0
09/14/85	0800-1200	56.08	30.82	25.3
09/14/85	1200-1600	63.94	16.54	47.4
09/14/85	1600-2000	35.48	4.26	31.2
09/14/85	2000-2400	8.36	1.85	6.5
09/15/85	0000-0600	6.50	3.48	3.0
09/15/85	0800-1200	46.08	30.0	16.1
09/15/85	1200-1600	28.76	10.45	18.3
09/15/85	1600-2000	13.16	3.52	9.6
09/15/85	2000-2400	6.06	5.36	0.7
09/16/85	0000-0600	6.81	5.78	1.0
09/16/85	0800-1200	28.30	22.42	5.9
09/16/85	1200-1600	21.86	12.74	9.1
09/16/85	1600-2000	8.68	3.20	5.5
09/16/85	2000-2400	5.92	4.30	1.6
09/17/85	0000-0600	11.4	9.46	1.9
09/17/85	0800-1200	29.95	23.86	6.1
09/17/85	1200-1600	24.57	14.45	10.1
09/17/85	1600-2000	10.31	4.77	5.5
09/17/85	2000-2400	3.57	2.76	0.8
09/18/85	0000-0600	2.92	2.34	0.6
09/18/85	0800-1200	2.76	2.08	0.7
09/18/85	1200-1600	4.03	2.18	1.9
09/18/85	1600-2000	1.94	0.79	1.2
09/18/85	2000-2400	1.93	1.60	0.3
09/19/85	0000-0600	1.61	1.36	0.3

[a] No data.

TABLE 14

LISTING OF DENUDER DIFFERENCE METHOD RESULTS ($nMol/M^3$)

DATE	PERIOD (PDT)	TOTAL FINE NO_3^-	FINE PARTIC. NO_3^-	HNO_3
09/11/85	0800-1200	42.42	26.0	16.1
09/11/85	1200-1600	123.55	37.4	85.5
09/11/85	1600-2000	83.55	28.9	54.8
09/11/85	2000-2400	29.35	10.5	19.4
09/12/85	0000-0600	46.61	30.0	16.1
09/12/85	0800-1200	229.19	117	113
09/12/85	1200-1600	334.68	197	139
09/12/85	1600-2000	601.13	237	364
09/12/85	2000-2400	275.00	142	132
09/13/85	0000-0600	170.32	115	54.8
09/13/85	0800-1200	383.23	----[a]	---[a]
09/13/85	1200-1600	599.19	160	439
09/13/85	1600-2000	640.81	145	497
09/13/85	2000-2400	238.23	74.5	165
09/14/85	0000-0600	264.03	152	113
09/14/85	0800-1200	904.52	497	408
09/14/85	1200-1600	1031.29	267	765
09/14/85	1600-2000	572.26	68.7	503
09/14/85	2000-2400	134.84	29.8	105
09/15/85	0000-0600	104.84	56.1	48.4
09/15/85	0800-1200	743.23	484	260
09/15/85	1200-1600	463.87	169	295
09/15/85	1600-2000	212.26	56.8	155
09/15/85	2000-2400	97.74	86.5	11.3
09/16/85	0000-0600	109.84	93.2	16.1
09/16/85	0800-1200	456.45	362	95.2
09/16/85	1200-1600	352.58	206	147
09/16/85	1600-2000	140.00	51.6	88.7
09/16/85	2000-2400	95.48	69.4	25.8
09/17/85	0000-0600	183.87	153	30.6
09/17/85	0800-1200	483.06	385	98.4
09/17/85	1200-1600	396.29	233	163
09/17/85	1600-2000	166.29	76.9	88.7
09/17/85	2000-2400	57.58	44.5	12.9
09/18/85	0000-0600	47.09	37.7	9.7
09/18/85	0800-1200	44.52	33.6	11.3
09/18/85	1200-1600	65.00	35.2	30.6
09/18/85	1600-2000	31.29	12.7	19.4
09/18/85	2000-2400	31.13	25.8	4.8
09/19/85	0000-0600	25.97	21.9	4.8

[a] No data.

to retain HONO efficiently (12). The IC peak for $SO_3^{=}$, which might result from filter SO_2 retention (11) without oxidation to $SO_4^{=}$, occurs at nearly the same retention time, increasing the uncertainty of these results.

It is reported (9) that the IC, itself, can generate NO_2^- from samples containing NO_3^-. However, analysis of nylon filters spiked with $NaNO_3$ showed only trace levels of apparent NO_2^-.

Apparent NO_2^- results are shown in Table 15, based on determinations with both the fine particulate NO_3^- (FPN) and fine total inorganic NO_3^- (TFIN) samplers. It is expected that HONO would be at least partially removed in passage through an MgO-coated denuder. Nevertheless, in some cases, the measured NO_2^- was greater on the FPN than on the TFIN sampler. Furthermore, although nighttime levels generally exceeded those for daytime, the latter were frequently substantial; this is inconsistent with HONO as a source of this measurement.

In summary, the results for apparent HONO are highly uncertain and would require further investigation to confirm the measurement. These results are included only for comparison with HONO measurements by better techniques. Retention of NO_2 and/or SO_2 with the present batch of Nylon filters also remains a possible source of these peaks.

E. Ammonia and Particulate Ammonium Measured by the Filter Pack Method

Tables 16 and 17 lists values (in $\mu g/m^3$ and nmoles/m^3, respectively) for the period 0800 hours, 9/11 through 0600 hours, 9/19/85 for gaseous NH_3 and particulate NH_4^+.

F. Ammonia by the Denuder Tube Method

Table 18 lists values (in $\mu g/m^3$ and nmoles/m^3) for NH_3 obtained with 10 or 12 hours denuder tube samplers throughout the period 0800 hours, 9/11 to 0600 hours, 9/19/85.

TABLE 15

Nylon Filter Sample Estimates of Apparent Nitrous Acid ($\mu g\ NO_2^-/m^3$)

Date	Period	NO_2^- on Particulate NO_3^- Sampler	NO_2^- on Total NO_3^- Sampler
9/11/85	0800 - 1200	0.8	0.4
	1200 - 1600	< 0.4	< 0.4
	1600 - 2000	< 0.4	2.6
	2000 - 2400	< 0.4	4.0
9/12/85	0000 - 0600	< 0.3	2.4
	0800 - 1200	< 0.4	2.1[a]
	1200 - 1600	1.6[a]	1.2[a]
	1600 - 2000	1.8[a]	0.9[a]
	2000 - 2400	2.2	2.3[a]
9/13/85	0000 - 0600	1.6	1.2[a]
	0800 - 1200	-	< 0.4
	1200 - 1600	1.6	< 0.4
	1600 - 2000	2.2	< 0.4
	2000 - 2400	2.9	0.9[a]
9/14/85	0000 - 0600	2.1	1.9[a]
	0800 - 1200	< 0.4	2.1
	1200 - 1600	< 0.4	1.9
	1600 - 2000	< 0.4	1.9
	2000 - 2400	< 0.4	2.8
9/15/85	0000 - 0600	< 0.4	1.7
	0800 - 1200	0	2.3
	1200 - 1600	0	1.4
	1600 - 2000	0	1.4
	2000 - 2400	< 0.4	2.3
9/16/85	0000 - 0600	< 0.4	1.0
	0800 - 1200	< 0.4	< 0.5
	1200 - 1600	< 0.4	< 0.5
	1600 - 2000	1.4	< 0.5
	2000 - 2400	< 0.4	0.9[a]

(Continued on Next Page)

a. Uncertain whether NO_2^- or $SO_3^=$.

TABLE 15 Continued

Nylon Filter Sample Estimates of Apparent Nitrous Acid (µg NO_2^-/m^3)

Date	Period	NO_2^- on Particulate NO_3^- Sampler	NO_2^- on Total NO_3^- Sampler
9/17/85	0000 - 0600	< 0.4	0.8[a]
	0800 - 1200	< 0.4	0.9
	1200 - 1600	< 0.4	0.9
	1600 - 2000	< 0.4	0.9
	2000 - 2400	< 0.4	0.9
9/18/85	0000 - 0600	< 0.4	1.2
	0800 - 1200	< 0.4	1.4
	1200 - 1600	0	1.4
	1600 - 2000	0	1.6
	2000 - 2400	0	3.3
9/19/85	0000 - 0600	< 0.4	1.5

a. Uncertain whether NO_2^- or $SO_3^{=}$.

TABLE 16

LISTING OF FILTER PACK PARTICULATE AMMONIUM

AND GASEOUS AMMONIA RESULTS (Ug/m³)

DATE	PERIOD (PDT)	PARTICULATE NH_4^+	NH_3 AS NH_4^+
09/11/85	0800-1200	0.56	2.68
09/11/85	1200-1600	0.97	3.34
09/11/85	1600-2000	1.02	3.13
09/11/85	2000-2400	0.63	3.19
09/12/85	0000-0600	1.27	3.20
09/12/85	0800-1200	2.34	5.55
09/12/85	1200-1600	2.58	25.7
09/12/85	1600-2000	3.65	7.60
09/12/85	2000-2400	3.00	5.24
09/13/85	0000-0600	1.77	4.24
09/13/85	0800-1200	2.62	12.2
09/13/85	1200-1600	1.86	9.48
09/13/85	1600-2000	3.11	7.01
09/13/85	2000-2400	2.06	4.30
09/14/85	0000-0600	3.45	3.55
09/14/85	0800-1200	3.58	4.59
09/14/85	1200-1600	3.86	5.39
09/14/85	1600-2000	1.82	4.54
09/14/85	2000-2400	1.63	3.49
09/15/85	0000-0600	1.94	2.78
09/15/85	0800-1200	3.73	6.65
09/15/85	1200-1600	1.87	7.76
09/15/85	1600-2000	2.01	3.67
09/15/85	2000-2400	2.83	3.96
09/16/85	0000-0600	3.74	2.31
09/16/85	0800-1200	11.71	17.3
09/16/85	1200-1600	3.55	7.18
09/16/85	1600-2000	1.58	2.74
09/16/85	2000-2400	3.63	2.01
09/17/85	0000-0600	6.23	3.01
09/17/85	0800-1200	2.89	-----[A]
09/17/85	1200-1600	4.52	7.23
09/17/85	1600-2000	2.38	2.70
09/17/85	2000-2400	1.99	2.61
09/18/85	0000-0600	1.69	1.99
09/18/85	0800-1200	1.34	2.09
09/18/85	1200-1600	1.01	1.31
09/18/85	1600-2000	0.49	1.78
09/18/85	2000-2400	0.92	2.55
09/19/85	0000-0600	0.83	1.06

[A] Bad sample.

TABLE 17

LISTING OF FILTER PACK PARTICULATE AMMONIUM

AND GASEOUS AMMONIA RESULTS (nMol/m³)

DATE	PERIOD (PDT)	PARTICULATE NH_4^+	NH_3
09/11/85	0800-1200	31.11	148.89
09/11/85	1200-1600	53.89	185.56
09/11/85	1600-2000	56.67	173.89
09/11/85	2000-2400	35.00	177.22
09/12/85	0000-0600	70.56	177.78
09/12/85	0800-1200	130.00	308.33
09/12/85	1200-1600	143.33	1427.78
09/12/85	1600-2000	202.78	422.22
09/12/85	2000-2400	166.67	291.11
09/13/85	0000-0600	98.33	235.56
09/13/85	0800-1200	145.56	677.78
09/13/85	1200-1600	103.33	526.67
09/13/85	1600-2000	172.78	389.44
09/13/85	2000-2400	114.44	238.89
09/14/85	0000-0600	191.67	197.22
09/14/85	0800-1200	198.89	255.00
09/14/85	1200-1600	214.44	299.44
09/14/85	1600-2000	101.11	252.22
09/14/85	2000-2400	90.56	193.89
09/15/85	0000-0600	107.78	154.44
09/15/85	0800-1200	207.22	369.44
09/15/85	1200-1600	103.89	431.11
09/15/85	1600-2000	111.67	203.89
09/15/85	2000-2400	157.22	220.00
09/16/85	0000-0600	207.78	128.33
09/16/85	0800-1200	650.56	961.11
09/16/85	1200-1600	197.22	398.89
09/16/85	1600-2000	87.78	152.22
09/16/85	2000-2400	201.67	111.67
09/17/85	0000-0600	346.11	167.22
09/17/85	0800-1200	160.56	----[A]
09/17/85	1200-1600	251.11	401.67
09/17/85	1600-2000	132.22	150.00
09/17/85	2000-2400	110.56	145.00
09/18/85	0000-0600	93.89	110.56
09/18/85	0800-1200	74.44	116.11
09/18/85	1200-1600	56.11	72.78
09/18/85	1600-2000	27.22	98.89
09/18/85	2000-2400	51.11	141.67
09/19/85	0000-0600	46.11	58.89

[A] Bad sample.

TABLE 18

LISTING OF GASEOUS AMMONIA RESULTS BY

OXALIC ACID DENUDER TUBE COLLECTION

STARTING DATE	PERIOD (PDT)	Ug/m^3 as NH_4^+	nMol/m^3
09/11/85	0800-2000	2.0	111
09/11/85	2000-0600	1.4	77.7
09/12/85	0800-2000	10.3	572
09/12/85	2000-0600	2.4	133
09/13/85	0800-2000	6.2	344
09/13/85	2000-0600	2.0	111
09/14/85	0800-2000	3.0	167
09/14/85	2000-0600	1.4	77.7
09/15/85	0800-2000	3.3	183
09/15/85	2000-0600	---[A]	---[A]
09/16/85	0800-2000	7.2	400
09/16/85	2000-0600	2.1	117
09/17/85	0800-2000	8.3	461
09/17/85	2000-0600	0.9	50.0
09/18/85	0800-2000	---[A]	---[A]
09/18/85	2000-0600	3.2	178

[A] No data.

G. Ozone, Temperature and Relative Humidity

One-hour average values for O_3, T (^{o}C), and percent R.H. are given in Table 19. The highest 1-hour ozone value was 0.22 ppm, observed 1500-1600 hours on 9/14/85. Four of the eight sampling days exhibited maximum O_3 values of 0.1 - 0.2 ppm. Measured relative humidity values ranged from 15.7% to 9/14/85 at 1500-1600 hours to 83%, 0500-0600 hours, 9/16/85. As noted in Section IV-I, the R.H. values are too low, at least for readings $\leq$ 40% R.H. Temperature ranged from 14.5 ^{o}C, 0300-0400 hours 9/19/85 to 33.7 ^{o}C at 1400-1500 hours, 9/14/85.

H. High Volume Filter Sample Results for Nitrate and Sulfate

1. Experimental

Three high volume filter samplers were calibrated for flow and operated by the ARB staff. One unit was equipped with an inlet permitting collection of $\leq$ 10 μm particles (a "PM-10" sampler). The other two units were in standard housings sampling without additional size discrimination. All employed 8" x 10" filters. Filter media and analyses were provided by the present authors. One conventional hi-vol and the PM-10 sampler employed Whatman QMA filters described as "High Purity Quartz Microfibre". These were from the lot number 49440 BJ and were from a set of 130,000 filters shipped to the EPA for nationwide PM-10 sampling in 1985. The second conventional hi-vol employed Whatman EPM 2000 filters described as "High Purity Glass Microfibre". These were from Lot NO. 49491 AG and were from a shipment to the EPA of 50,000 filters for use for TSP measurement in the National Air Surveillance Network in 1985.

An EPA-sponsored evaluation of the glass fiber filters at AIHL demonstrated a maximum potential positive sulfate artifact of 13 $\mu g/m^3$ (assuming 1500 m^3 air volumes). With the quartz filter, the maximum 24 hr sulfate was 5.1 $\mu g/m^3$ (13). The glass fiber filters used exhibited very high capacities for HNO_3 retention at 50% R.H. (e.g., > 600 μg/47 mm filter)

TABLE 19

Listing of Ozone Concentration, Relative Humidity, and Temperature

(One Hour Average Values)

Date	Period (PDT)	O_3(ppm)	T(C)	R.H. (%)
09/11/85	2300-2400	0.0099	23.82	35.07
09/12/85	0000-0100	0.0111	24.00	34.77
09/12/85	0100-0200	0.0107	24.10	34.71
09/12/85	0200-0300	0.0107	24.14	35.86
09/12/85	0300-0400	0.0107	24.24	34.77
09/12/85	0400-0500	0.0107	24.34	33.62
09/12/85	0500-0600	0.0115	24.51	33.30
09/12/85	0600-0700	0.0082	23.09	34.93
09/12/85	0700-0800	0.0124	21.31	40.85
09/12/85	0800-0900	0.0089	19.81	44.43
09/12/85	0900-1000	0.0115	19.68	45.28
09/12/85	1000-1100	0.0127	18.83	43.99
09/12/85	1100-1200	0.0148	19.52	36.41
09/12/85	1200-1300	0.0138	20.84	27.51
09/12/85	1300-1400	0.0575	21.75	19.76
09/12/85	1400-1500	0.0669	23.65	22.20
09/12/85	1500-1600	0.0957	27.09	27.01
09/12/85	1600-1700	0.1179	28.64	22.99
09/12/85	1700-1800	0.1329	27.06	23.81
09/12/85	1800-1900	0.1242	25.65	26.49
09/12/85	1900-2000	0.0774	24.31	26.99
09/12/85	2000-2100	0.0236	22.59	35.39
09/12/85	2100-2200	0.0078	20.84	46.14
09/12/85	2200-2300	0.0137	19.77	47.30
09/12/85	2300-2400	0.0093	19.22	47.60
09/13/85	0000-0100	0.0093	18.71	48.35
09/13/85	0100-0200	0.0239	18.26	44.37
09/13/85	0200-0300	0.0268	17.97	45.21
09/13/85	0300-0400	0.0305	17.52	43.86
09/13/85	0400-0500	0.0299	17.10	42.97
09/13/85	0500-0600	0.0280	16.87	42.50
09/13/85	0600-0700	0.0142	16.55	40.81
09/13/85	0700-0800	0.0103	17.92	39.73
09/13/85	0800-0900	0.0188	21.87	27.53
09/13/85	0900-1000	0.0325	24.31	20.77
09/13/85	1000-1100	0.0547	26.80	18.59
09/13/85	1100-1200	0.0620	27.82	17.37
09/13/85	1200-1300	0.0781	30.17	14.57
09/13/85	1300-1400	0.1122	32.10	59.61
09/13/85	1400-1500	0.1328	32.14	62.95
09/13/85	1500-1600	0.1452	29.51	27.75
09/13/85	1600-1700	0.1705	33.36	17.58
09/13/85	1700-1800	0.1588	30.65	20.53
09/13/85	1800-1900	0.1122	27.40	21.77
09/13/85	1900-2000	0.0681	24.43	25.23
09/13/85	2000-2100	0.0362	22.55	28.11
09/13/85	2100-2200	0.0129	21.39	31.73
09/13/85	2200-2300	0.0083	19.58	39.09
09/13/85	2300-2400	0.0121	18.63	43.78

TABLE 19 (Contd.)

Date	Period (PDT)	O_3(ppm)	T(C)	R.H. (%)
09/14/85	0000-0100	0.0212	18.10	43.77
09/14/85	0100-0200	0.0357	17.64	44.27
09/14/85	0200-0300	0.0295	17.75	46.74
09/14/85	0300-0400	0.0255	16.95	46.21
09/14/85	0400-0500	0.0270	16.70	45.98
09/14/85	0500-0600	0.0224	16.66	45.19
09/14/85	0600-0700	0.0234	16.69	42.56
09/14/85	0700-0800	0.0330	17.18	41.66
09/14/85	0800-0900	0.0307	21.53	32.83
09/14/85	0900-1000	0.0441	24.68	26.75
09/14/85	1000-1100	0.0819	27.33	22.63
09/14/85	1100-1200	0.1162	30.61	16.99
09/14/85	1200-1300	0.1308	32.14	16.67
09/14/85	1300-1400	0.1465	32.66	14.55
09/14/85	1400-1500	0.1512	33.74	13.09
09/14/85	1500-1600	0.2214	33.18	15.70
09/14/85	1600-1700	0.1919	31.23	20.22
09/14/85	1700-1800	0.1116	29.27	20.06
09/14/85	1800-1900	0.0744	26.48	24.62
09/14/85	1900-2000	0.0584	23.47	34.28
09/14/85	2000-2100	0.0428	21.82	40.49
09/14/85	2100-2200	0.0148	20.50	46.42
09/14/85	2200-2300	0.0060	18.93	51.91
09/14/85	2300-2400	0.0076	18.17	54.09
09/15/85	0000-0100	0.0163	17.89	51.91
09/15/85	0100-0200	0.0415	17.58	50.16
09/15/85	0200-0300	0.0327	17.13	53.80
09/15/85	0300-0400	0.0326	16.67	54.44
09/15/85	0400-0500	0.0210	16.44	57.58
09/15/85	0500-0600	0.0349	16.00	52.89
09/15/85	0600-0700	0.0408	15.90	52.44
09/15/85	0700-0800	0.0248	16.65	54.85
09/15/85	0800-0900	0.0378	20.36	45.97
09/15/85	0900-1000	0.0497	23.27	36.97
09/15/85	1000-1100	0.0840	26.28	28.79
09/15/85	1100-1200	0.1110	29.01	22.46
09/15/85	1200-1300	0.1207	31.17	19.41
09/15/85	1300-1400	0.1279	31.72	23.28
09/15/85	1400-1500	0.1213	31.37	26.66
09/15/85	1500-1600	0.0998	30.35	31.40
09/15/85	1600-1700	0.0791	29.26	30.89
09/15/85	1700-1800	0.0823	27.72	34.38
09/15/85	1800-1900	0.0964	25.21	47.74
09/15/85	1900-2000	0.0407	22.22	54.19
09/15/85	2000-2100	0.0234	20.32	58.99
09/15/85	2100-2200	0.0115	19.17	65.93
09/15/85	2200-2300	0.0102	18.48	66.86
09/15/85	2300-2400	0.0074	17.73	69.35

TABLE 19 (Contd.)

Date	Period (PDT)	O_3(ppm)	T(C)	R.H. (%)
09/16/85	0000-0100	0.0065	16.81	72.11
09/16/85	0100-0200	0.0152	16.35	73.16
09/16/85	0200-0300	0.0206	16.04	73.85
09/16/85	0300-0400	0.0142	15.95	75.64
09/16/85	0400-0500	0.0159	15.72	79.20
09/16/85	0500-0600	0.0152	16.15	83.05
09/16/85	0600-0700	0.0162	16.34	80.17
09/16/85	0700-0800	0.0216	16.58	77.24
09/16/85	0800-0900	0.0211	17.68	73.15
09/16/85	0900-1000	0.0207	19.10	68.55
09/16/85	1000-1100	0.0421	21.14	60.24
09/16/85	1100-1200	0.0725	24.03	47.78
09/16/85	1200-1300	0.0868	26.47	38.70
09/16/85	1300-1400	0.0781	28.14	33.08
09/16/85	1400-1500	0.0781	28.14	33.08
09/16/85	1500-1600	xxxxxx	xxxxx	xxxxx
09/16/85	1600-1700	xxxxxx	xxxxx	xxxxx
09/16/85	1700-1800	xxxxxx	xxxxx	xxxxx
09/16/85	1800-1900	xxxxxx	xxxxx	xxxxx
09/16/85	1900-2000	xxxxxx	xxxxx	xxxxx
09/16/85	2000-2100	xxxxxx	xxxxx	xxxxx
09/16/85	2100-2200	xxxxxx	xxxxx	xxxxx
09/16/85	2200-2300	xxxxxx	xxxxx	xxxxx
09/16/85	2300-2400	xxxxxx	xxxxx	xxxxx
09/17/85	0000-0100	xxxxxx	xxxxx	xxxxx
09/17/85	0100-0200	xxxxxx	xxxxx	xxxxx
09/17/85	0200-0300	xxxxxx	xxxxx	xxxxx
09/17/85	0300-0400	xxxxxx	xxxxx	xxxxx
09/17/85	0400-0500	xxxxxx	xxxxx	xxxxx
09/17/85	0500-0600	xxxxxx	xxxxx	xxxxx
09/17/85	0600-0700	xxxxxx	xxxxx	xxxxx
09/17/85	0700-0800	xxxxxx	xxxxx	xxxxx
09/17/85	0800-0900	xxxxxx	xxxxx	xxxxx
09/17/85	0900-1000	xxxxxx	xxxxx	xxxxx
09/17/85	1000-1100	0.0640	24.56	42.55
09/17/85	1100-1200	xxxxxx	xxxxx	xxxxx
09/17/85	1200-1300	0.0778	27.18	29.63
09/17/85	1300-1400	0.0846	27.46	32.33
09/17/85	1400-1500	0.0963	27.45	33.48
09/17/85	1500-1600	0.0783	27.51	30.09
09/17/85	1600-1700	0.0679	27.10	32.86
09/17/85	1700-1800	0.0635	xxxxx	43.06
09/17/85	1800-1900	0.0451	xxxxx	49.81
09/17/85	1900-2000	0.0364	xxxxx	56.57
09/17/85	2000-2100	0.0103	19.11	59.41
09/17/85	2100-2200	0.0068	18.06	62.86
09/17/85	2200-2300	0.0070	17.07	68.35
09/17/85	2300-2400	0.0120	16.34	72.53

TABLE 19 (Contd.)

Date	Period (PDT)	O_3(ppm)	T(C)	R.H. (%)
09/18/85	0000-0100	0.0014	15.66	76.78
09/18/85	0100-0200	0.0121	15.71	75.98
09/18/85	0200-0300	0.0095	15.76	74.31
09/18/85	0300-0400	0.0076	15.39	73.92
09/18/85	0400-0500	0.0086	15.26	71.92
09/18/85	0500-0600	0.0075	15.60	67.20
09/18/85	0600-0700	0.0071	15.71	68.33
09/18/85	0700-0800	0.0090	15.48	71.95
09/18/85	0800-0900	0.0132	15.56	71.24
09/18/85	0900-1000	0.0169	15.80	73.53
09/18/85	1000-1100	0.0109	15.76	74.78
09/18/85	1100-1200	0.0257	16.48	68.16
09/18/85	1200-1300	0.0290	17.57	58.45
09/18/85	1300-1400	0.0192	15.56	74.31
09/18/85	1400-1500	0.0325	18.50	57.80
09/18/85	1500-1600	0.0279	18.72	51.82
09/18/85	1600-1700	0.0179	17.49	52.84
09/18/85	1700-1800	0.0193	18.56	50.54
09/18/85	1800-1900	0.0217	18.64	48.35
09/18/85	1900-2000	0.0080	17.69	52.70
09/18/85	2000-2100	0.0077	16.83	60.16
09/18/85	2100-2200	0.0088	16.42	64.92
09/18/85	2200-2300	0.0079	15.86	62.78
09/18/85	2300-2400	0.0086	15.45	62.48
09/19/85	0000-0100	0.0106	15.30	61.63
09/19/85	0100-0200	0.0109	14.96	61.53
09/19/85	0200-0300	0.0126	14.73	61.76
09/19/85	0300-0400	0.0135	14.46	61.72
09/19/85	0400-0500	0.0124	14.60	61.87
09/19/85	0500-0600	0.0101	15.55	61.73
09/19/85	0600-0700	0.0068	13.04	48.23

(13). Prior studies have compared hi-vol sampler (glass fiber filter) nitrate to the sum of atmospheric HNO_3 and particulate NO_3^- (1,14). In short term sampling in Souther California and in 24 hr sampling elsewhere, equivalent results were obtained indicating that the glass fiber filters retained both particulate and gaseous NO_3^- quantitively. At the high HNO_3 dosages observed in the South Coast Air Basin, comparisons between 24 hr hi-vol and true sum of HNO_3 plus particulate NO_3 demonstrated 20-40% HNO_3 penetration through glass fiber filters similar to those described here (14).

For Whatman QMA ("quartz") filters, the capacity for HNO_3 was about 185 μg/47 mm disc, or about 3 $\mu g/m^3$ for a 24 hr hi-vol sampler. It is expected that atmospheric NO_3^- results on quartz fiber will be lower than those on parallel glass fiber filters because of lower capacity for atmospheric HNO_3 retention and greater loss of NO_3^- as HNO_3 by volatilization of NH_4NO_3. Similarly, the much greater retention of SO_2 on glass fiber causes higher levels of apparent sulfate compared to levels with quartz fiber filters (15).

2. Results

Table 20 lists results for the three samplers and, for comparison, total fine NO_3^- and true fine particulate both measured with the DDM samplers. Comparison between the quartz and glass fiber filter hi-vols shows, as expected, much higher results on the glass fiber for both NO_3^- and $SO_4^=$. PM-10 results are consistently lower than those for the quartz filter hi-vol (Figure 8), reflecting the combined influence of the exclusion of > 10 μm particulate NO_3^- and at least partial removal of HNO_3 in the PM-10 sampler inlet.

Direct comparison of glass fiber hi-vol NO_3^- with total fine NO_3^- (i.e., HNO_3 plus fine particle NO_3^-) is difficult because of the significance of > 2.5 μm NO_3^-. Coarse particulate NO_3^- values were provided by parallel measurements of W. John et. al., (16) employing a dichotomous sampler. The last column in the table combines total fine NO_3^- with these coarse

TABLE 20

High Volume and PM-10 Sampler Nitrate and Sulfate Results ($\mu g/m^3$)[a]

Day	HiVol (Quartz)		HiVol (Glass Fiber)		PM-10 (Quartz)		True Fine Particulate NO_3^-	HNO_3 (DDM)	Total NO_3^-[b]	True Particulate NO_3^-
	NO_3^-	$SO_4^=$	NO_3^-	$SO_4^=$	NO_3^-	$SO_4^=$				
1	4.66	3.39	5.50	4.82	3.68	3.27	1.67	2.25	6.42	4.16
2	6.88	6.04	20.2	6.15	3.86	5.43	9.76	9.34	22.9	13.6
3	8.10	7.48	24.5	7.99	4.80	6.72	8.4[c]	16.8	27.9	10.9
4	5.80	5.72	22.2	5.26	3.42	5.17	10.7	20.9	34.6	13.7
5	4.23	5.85	18.5	5.74	2.19	4.85	10.5	8.41	25.9	17.4
6	4.44	5.09	19.5	5.47	3.14	4.55	10.3	4.54	24.4	19.8
7	6.28	4.82	19.9	4.85	4.50	4.39	9.0	4.25	19.0	14.8
8	4.50	3.52	8.32	4.55	2.52	3.14	1.6	0.82	4.52	3.74

a. The result are observed or calculated 22-hour average values.

b. The sum of true fine NO_3^-, HNO_3 and coarse NO_3^-, the latter calculated from results of W. John et al.

c. Results for 0800-1200 hr. are missing from average.

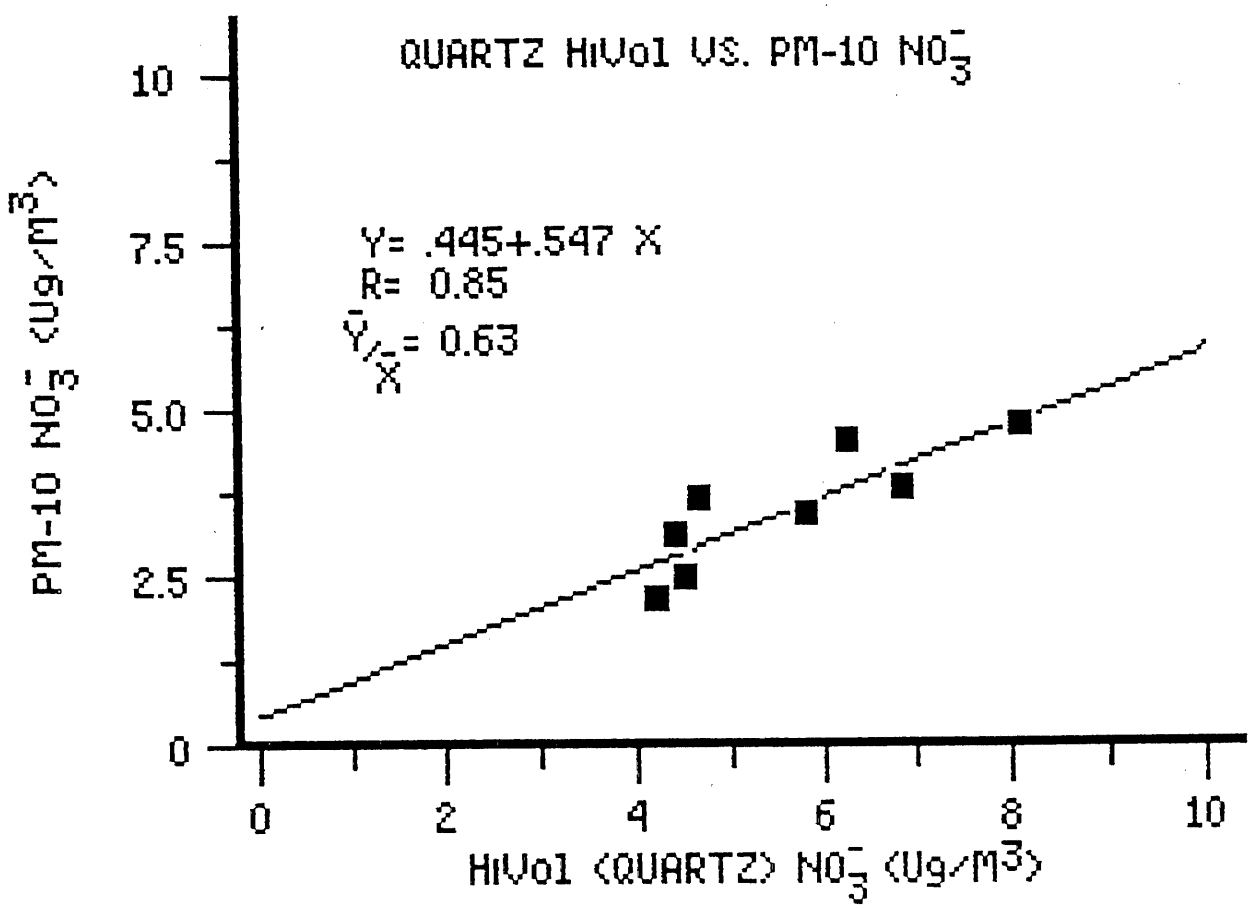

QUARTZ HiVol VS. PM-10 NO_3^-
Y= .445+.547 X
R= 0.85
$\bar{Y}/\bar{X}$= 0.63
PM-10 NO_3^- (Ug/M^3)
HiVol (QUARTZ) NO_3^- (Ug/M^3)
10
7.5
5.0
2.5
0
0
2
4
6
8
10

Figure 8

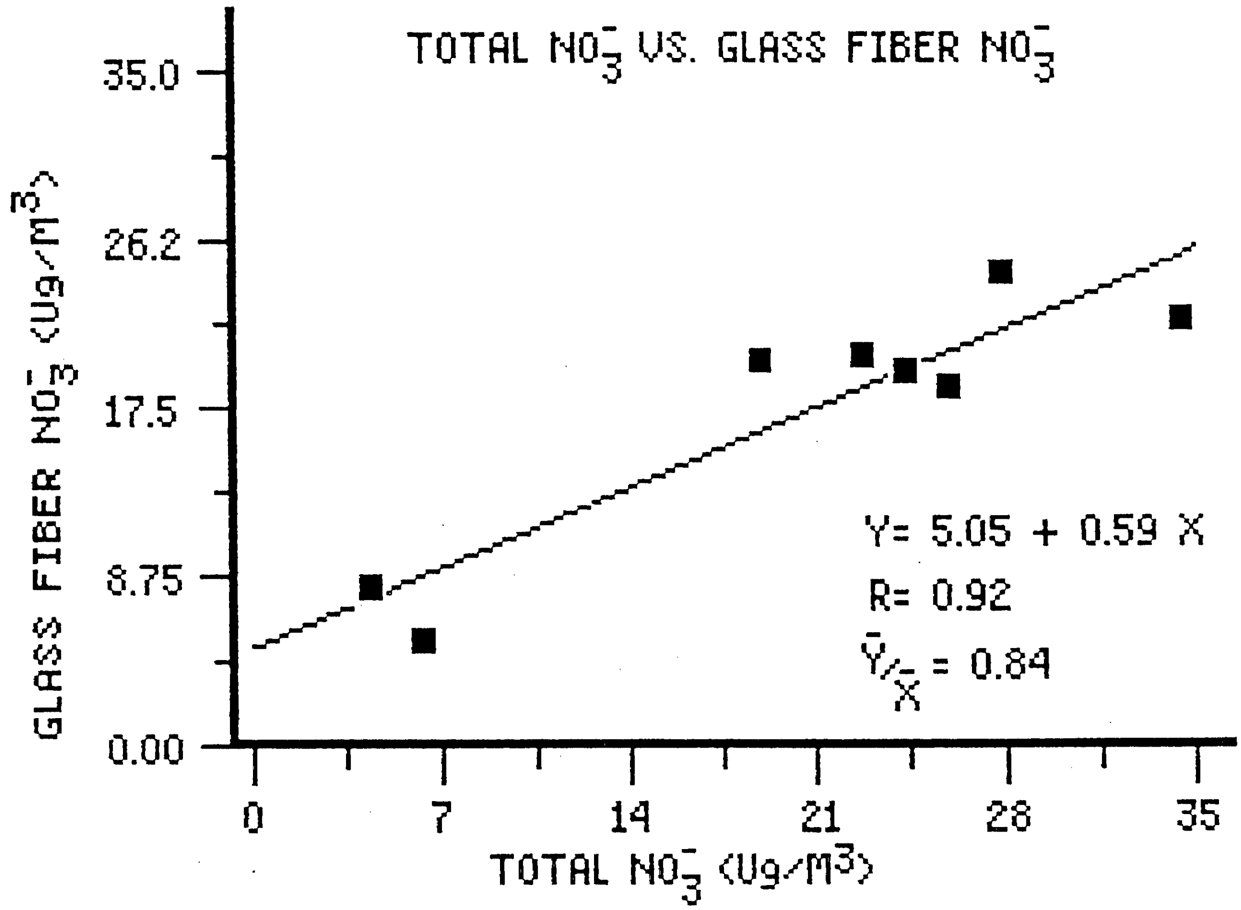
NO_3^- values. The coarse NO_3^- values were as much as 92% of the fine NO_3^-. The totals are then compared with hi-vol (glass fiber) NO_3^- in Figure 9) The difference in results can be interpreted as the partial loss of NO_3^- by penetration of atmospheric HNO_3 and/or that derived from NH_4NO_3 dissociation. Such loss averaged about 16% for these 22 hour NO_3^- collections.

Similarly, true fine particle NO_3^- from the DDM can be combined with coarse NO_3^- values to yield true particle NO_3^- values. These, in turn, are compared to hi-vol (quartz) values in Figure 10. No correlation is observed. The results suggest that the positive artifact due to HNO_3 retention on quartz is more than offset by volatilization of particulate NO_3^-. The recovered quartz fiber NO_3^- averages only about half of the true particulate NO_3^-.

A similar comparison of true particulate NO_3^- with hi-vol (glass fiber) NO_3^- values (Figure 11) leads to the conclusion that, except when HNO_3 levels are high, glass fiber NO_3^- provides a more reliable measure of particulate NO_3^- compared to quartz fiber filters. For the eight days sampled, the glass fiber NO_3^- values averaged about 40% too high.

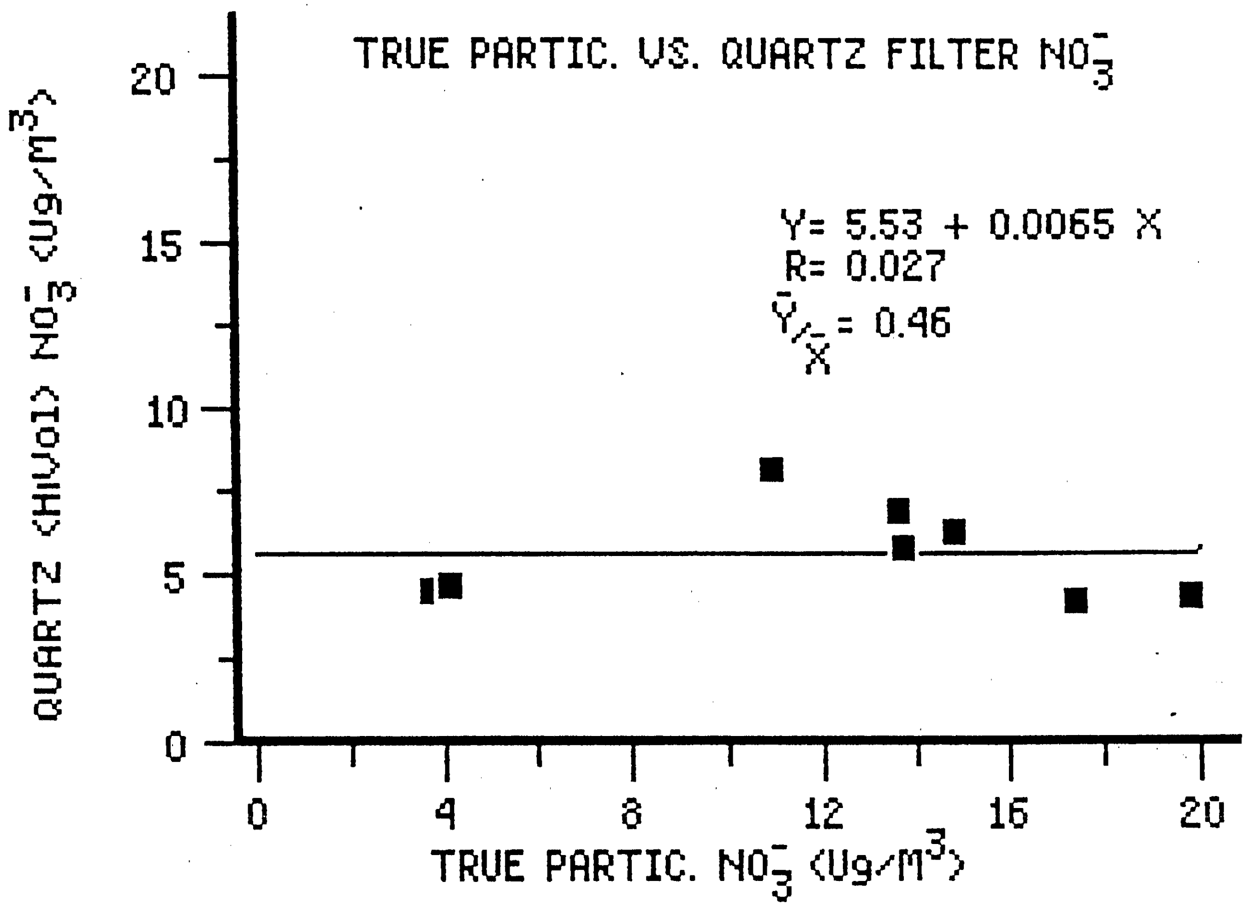
I. Apparent HCl Measurement

The Nylon filter samples from the DDM were analyzed by ion chromatography for Cl^- in addition to NO_3^-. On the assumption that HCl is retained on Nylon filters with an efficiency equal to that for HNO_3 sampler 3 (see Table 1) provides a measure of fine particulate chloride plus HCl. The corresponding analysis for sampler 2, employing an MgO-coated denuder, provides a measure of fine particulate chloride only, assuming the denuder removes HCl efficiently. With these assumptions, HCl is measured by difference, just as with HNO_3. Table 21 lists concentrations of total fine Cl^-, fine particulate Cl^- and the calculated HCl values. Apparent HCl results ranged from 0.2 to 4.1 $\mu g/m^3$. On five of the eight days the maximum was observed during the period 1200-1600 hours. Concentrations were generally lowest during the 0000-0600 hour periods.



TOTAL NO_3^- VS. GLASS FIBER NO_3^-
35.0
26.2
17.5
8.75
0.00
GLASS FIBER NO_3^- (Ug/M^3)
Y= 5.05 + 0.59 X
R= 0.92
$\bar{Y}/\bar{X}$ = 0.84
0
7
14
21
28
35
TOTAL NO_3^- (Ug/M^3)

Figure 9



TRUE PARTIC. VS. QUARTZ FILTER NO3-
Y= 5.53 + 0.0065 X
R= 0.027
Y/X = 0.46
QUARTZ (HIVol) NO3- (Ug/M3)
TRUE PARTIC. NO3- (Ug/M3)
0
5
10
15
20
0
4
8
12
16
20

Figure 10

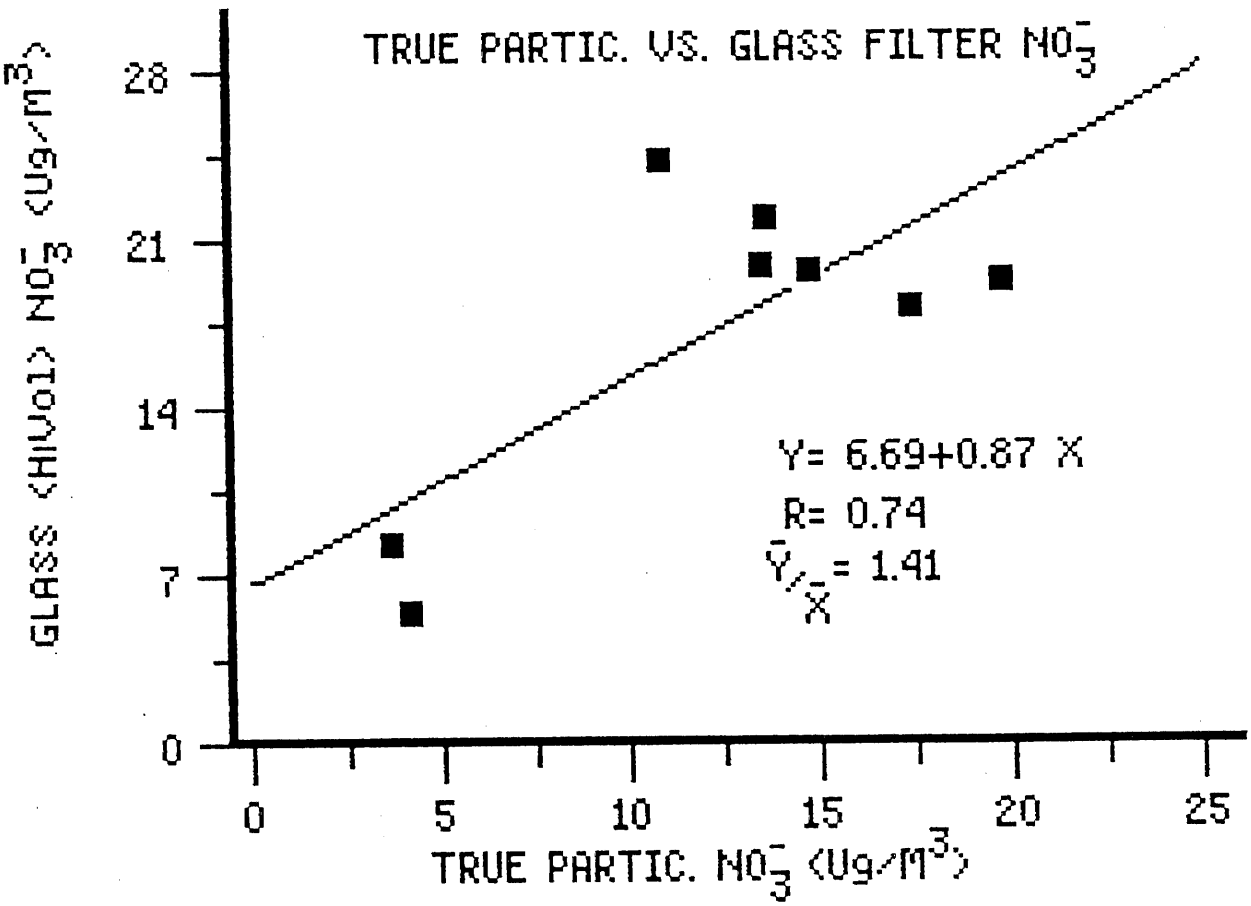

TRUE PARTIC. VS. GLASS FILTER NO_3^-
GLASS (HIVol) NO_3^- (Ug/M^3)
28
21
14
7
0
0
5
10
15
20
25
TRUE PARTIC. NO_3^- (Ug/M^3)
Y= 6.69+0.87 X
R= 0.74
$\bar{Y}/\bar{X}$= 1.41

Figure 11

TABLE 21

Concentrations of Chloride Species at Claremont ($\mu g/m^3$)

Date	Period[a]	Total Fine Cl^-	Fine Particulate Cl^-	Apparent HCl[b]
9/11/85	2	0.76	0.15	0.61
	3	2.60	-0.004	2.60
	4	1.46	0.10	1.36
	5	0.41	-0.11	0.41
9/12/85	1	0.26	0.07	0.19
	2	2.47	-0.004	2.47
	3	1.85	0.05	1.80
	4	2.74	-0.004	2.74
	5	0.64	-0.11	0.64
9/13/85	1	0.26	0.03	0.23
	2	1.91	--	--
	3	2.33	0.20	2.13
	4	3.12	0.05	3.07
	5	0.99	0.15	0.84
9/14/85	1	0.15	0.50	(-0.35)[c]
	2	3.26	0.47	2.79
	3	3.12	0.66	2.46
	4	2.93	0.37	2.56
	5	0.69	0.32	0.37
9/15/85	1	0.55	0.36	0.19
	2	2.33	0.47	1.86
	3	2.61	0.33	2.28
	4	1.78	0.37	1.41
	5	1.02	0.76	0.26
9/16/85	1	0.95	0.74	0.21
	2	2.54	2.30	0.24
	3	3.80	0.66	3.14
	4	2.08	0.57	1.51
	5	1.75	1.07	0.68
9/17/85	1	1.46	0.89	0.57
	2	2.68	0.22	2.46
	3	4.79	0.73	4.06
	4	2.02	0.70	1.32
	5	1.15	1.02	0.13

(Continued on next page)

TABLE 21 Continued

Concentrations of Chloride Species at Claremont ($\mu g/m^3$)

Date	Period[a]	Total Fine Cl^-	Fine Particulate Cl^-	Apparent HCl[b]
9/18/85	1	0.93	0.77	0.16
	2	1.21	0.83	0.38
	3	1.42	0.49	0.93
	4	0.93	0.39	0.54
	5	1.15	0.97	0.18
9/19/85	1	1.68	2.91	(-1.2)[c]

a. Period 1 00-06 hours
Period 2 08-12 hours
Period 3 12-16 hours
Period 4 16-20 hours
Period 5 20-24 hours

b. Since efficiency of HCl on nylon filters has not been determined, the accuracy of these results is unknown.

c. Considered invalid.

Relatively few measurements for atmospheric HCl have been made. In a previous ARB-sponsored study (2) we measured HCl by a filter pack technique in Riverside in September 1984. Concentrations of HCl ranged up to 3 $\mu g/m^3$.

Efficiency studies for HCl on nylon filters and in the MgO denuder are needed before the present results can be considered quantitative.

VI. ANALYSIS OF RESULTS

A. Comparison of Nitric Acid Results with the TAT, DDM and Tunable Diode Laser

Table 22 and the scatter diagram shown in Figure 12 compare TAT and DDM HNO_3 results for the period when both systems operated, 0800 hours, 9/14/85 to 0600 hours, 9/19/85. A large positive intercept is observed with only a moderate correlation coefficient (r=0.80). Average TAT results are significantly higher than those by the DDM except at the highest HNO_3 levels. This compares to results observed at Riverside (2) in September 1984 for which the regression equation was:

$$\begin{aligned} TAT &= 1.24 + 1.48\ DDM \\ r &= 0.94 \\ n &= 31 \end{aligned}$$

In that case, the relatively low intercept and high slope indicated about 50% higher TAT results throughout much of the HNO_3 range.

The present data comparison may also be assessed by time of day (Table 23 and Figure 13). Mean TAT/DDM ratios were calculated and plotted, together with standard deviations, excluding results for 0800 9/18 - 0600 9/19. The cause of the apparently inconsistent ratios may relate to the comparatively high relative humidity during this period. Rain was observed at the site on the morning of 9/18/85. This comparison suggests that the degree of agreement varies markedly depending on one or more of the variables, sunlight intensity, temperature and relative humidity. During daylight hours, average agreement was relatively good.

The pronounced day-night effect is similar to that reported by Anlauf et al., who observed a TAT/FP HNO_3 ratio up to two at night (10), but contrasts with the absence of such an effect in our Riverside results (2). The latter were obtained under conditions of relatively high temperature and low relative humidity, even during nighttime hours. The Claremont study was characterized by relatively large temperature and relative humidity differences from day to day and between daylight and nighttime periods.

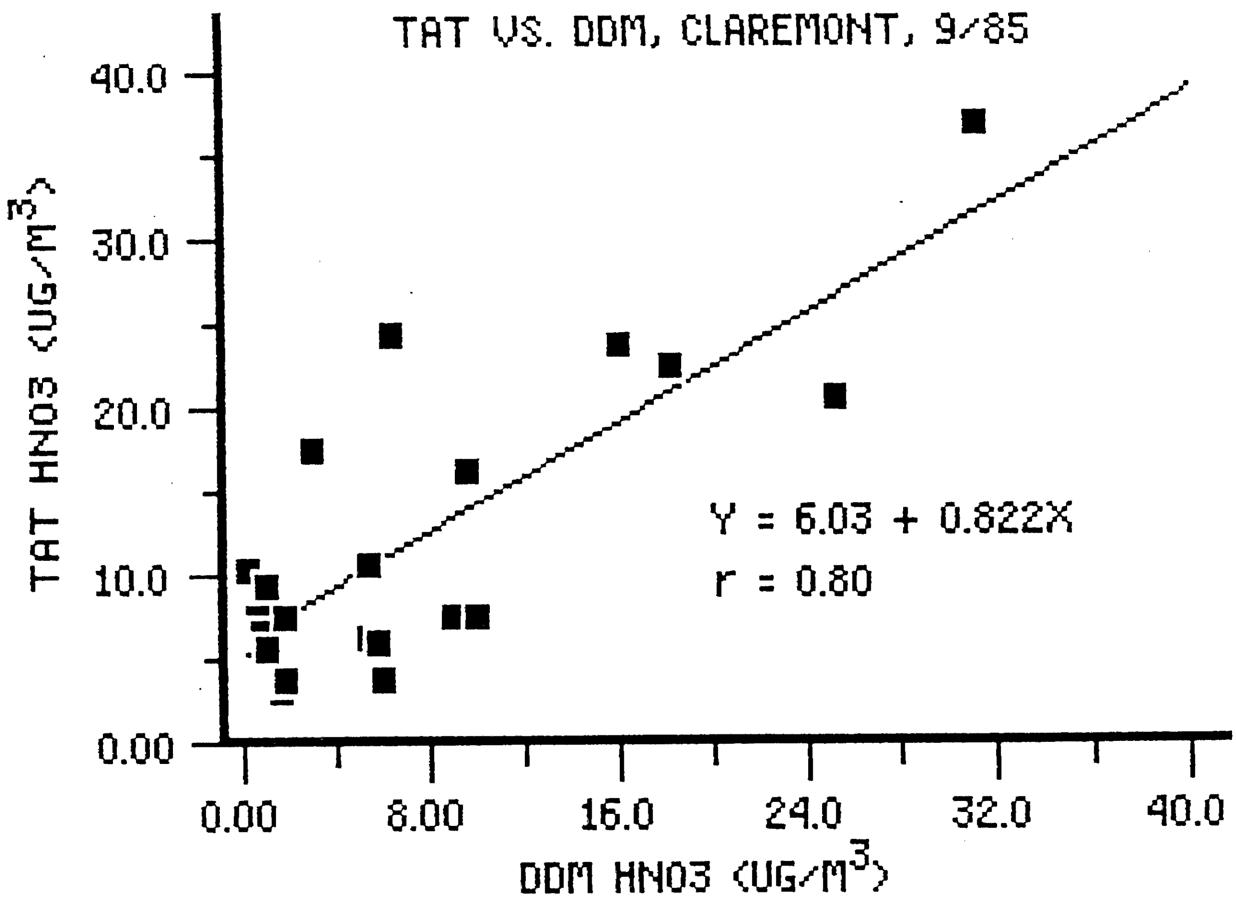
TABLE 22

COMPARISON OF TUNGSTIC ACID TECHNIQUE AND

DENUDER DIFFERENCE FOR NITRIC ACID (UG/M^3 AS NO_3^-)

DATE	PERIOD (PDT)	TAT[A]	DDM
09/14/85	0800-1200	20.5[B]	25.3
09/14/85	1200-1600	26.6[C]	47.4
09/14/85	1600-2000	36.9	31.2
09/14/85	2000-2400	24.3	6.5
09/15/85	0000-0600	17.4	3.0
09/15/85	0800-1200	23.6[D]	16.1
09/15/85	1200-1600	22.5	18.3
09/15/85	1600-2000	16.2	9.6
09/15/85	2000-2400	7.6	0.7
09/16/85	0000-0600	5.7	1.0
09/16/85	0800-1200	5.8[B]	5.9
09/16/85	1200-1600	7.6	9.1
09/16/85	1600-2000	6.4	5.5
09/16/85	2000-2400	3.2	1.6
09/17/85	0000-0600	3.8[E]	1.9
09/17/85	0800-1200	3.8	6.1
09/17/85	1200-1600	7.5	10.1
09/17/85	1600-2000	10.5[D]	5.5
09/17/85	2000-2400	6.4	0.8
09/18/85	0000-0600	5.9[E]	0.6
09/18/85	0800-1200	6.0	0.7
09/18/85	1200-1600	7.4	1.9
09/18/85	1600-2000	10.0	1.2
09/18/85	2000-2400	10.3	0.3
09/19/85	0000-0600	10.3	0.3

[A] Mean of four or six 1-hr average values except as noted
[B] Mean of two, 1-hr values
[C] Electronics saturated. Minimum value only
[D] Mean of three, 1-hr values
[E] Mean of five, 1-hr values



TAT VS. DDM, CLAREMONT, 9/85
40.0
30.0
20.0
10.0
0.00
TAT HNO3 (UG/M3)
Y = 6.03 + 0.822X
r = 0.80
0.00
8.00
16.0
24.0
32.0
40.0
DDM HNO3 (UG/M3)

Figure 12

TABLE 23

NITRIC ACID METHOD COMPARISON BY TIME OF DAY

TIME PERIOD (PDT)	DATE	TAT/DDM RATIO	MEAN RATIO[A]
0000-0600	9/15/85	5.8	
	9/16	5.7	
	9/17	2.0	5.8 ± 3.2
	9/18	9.8	
	9/19	34.3[B]	
0800-1200	9/14	0.81	
	9/15	1.47	
	9/16	0.98	0.97 ± 0.36
	9/17	0.62	
	9/18	8.57[B]	
1200-1600	9/14	0.56	
	9/15	1.23	
	9/16	0.84	0.88 ± 0.34
	9/17	0.74	
	9/18	3.89[B]	
1600-2000	9/14	1.18	
	9/15	1.69	
	9/16	1.16	1.49 ± 0.37
	9/17	1.91	
	9/18	7.83[B]	
2000-2400	9/14	3.74	
	9/15	10.9	
	9/16	2.00	6.2 ± 4.0
	9/17	8.00	
	9/18/85	34.3[B]	

[A] n=4, each case. Errors shown are one standard deviation.
[B] excluded from mean.

Ratio of HNO_3 Results by Time of Day

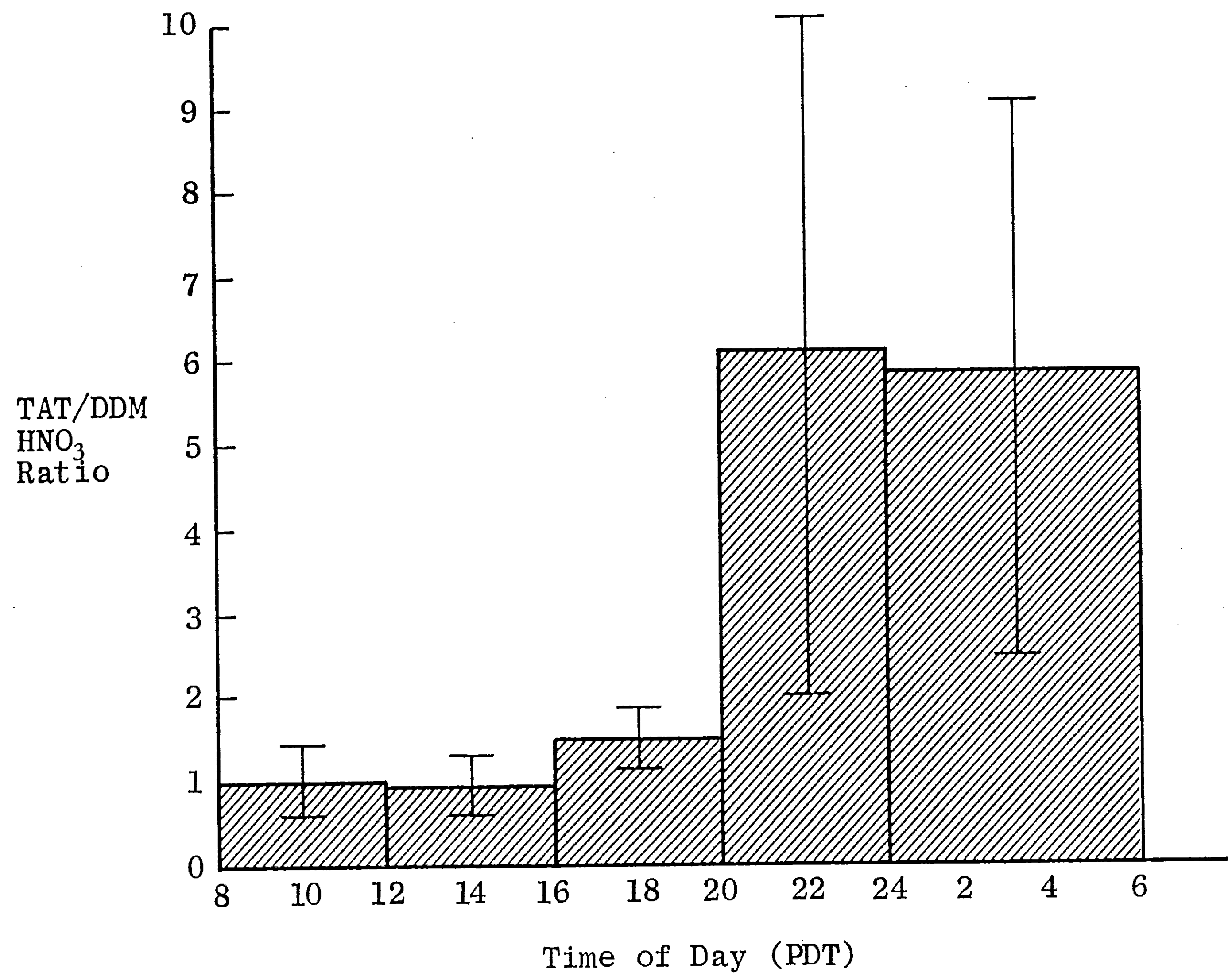


Figure 13

The present data are consistent with the more efficient collection on WO_x, relative to Nylon filters, of NO_x species other than HNO_3 especially during nighttime periods. Such additional species might include HONO, NO_3, N_2O_5 and perhaps organic nitrates and nitrites.

Nitric acid results with the TAT are plotted against hourly average O_3 concentrations in Figure 14. As in previous studies (1,2), a moderate correlation was observed.

The DDM results are compared to those the by tunable diode laser (TDL) in Table 24 and Figure 15. The TDL results are mean values, expressed in $\mu g/m^3$ (as NO_3^-), obtained by both G. Mackay and K. Anlauf, who operated separate TDL units. The difference in results may relate to losses in the inlet systems of both TDL units. Each sampled at 5 Lpm through separate 1/4" FEP Teflon lines consisting of an 8' section at atmospheric pressure, a 2 µm pore size Teflon filter and another 8' Teflon line section to the analyzer at below atmospheric pressure. Although no loss of HNO_3 in the inlet line was measurable in nearly anhydrous air, the loss was substantial in humidified air (17).

B. Comparison of Ammonia Results

Table 25 and Figure 16 compare NH_3 results by the TAT and the filter pack (FP) methods. To aid in data interpretation, the ratio of NH_3 results, FP/TAT, are plotted against mean temperature in Figure 17. The ratio ranges from 0.5 to 3, increasing with temperature. The results are tabulated by time of day in Table 26, showing higher ratios during daylight hours.

Ammonia sampling with oxalic acid-coated denuder tubes (DT) was assumed to provide an accurate measure of atmospheric NH_3. FP NH_3 values were averaged to permit the comparison with 10 or 12-hr DT results (Table 27 and Figure 18). The results are highly correlated (r=0.94) but the FP method, based on the ratio of means, averaged 50% higher than the DT. This is consistent with substantial volatilization of particulate NH_4^+ (as NH_3) from the prefilter in the FP sampler.

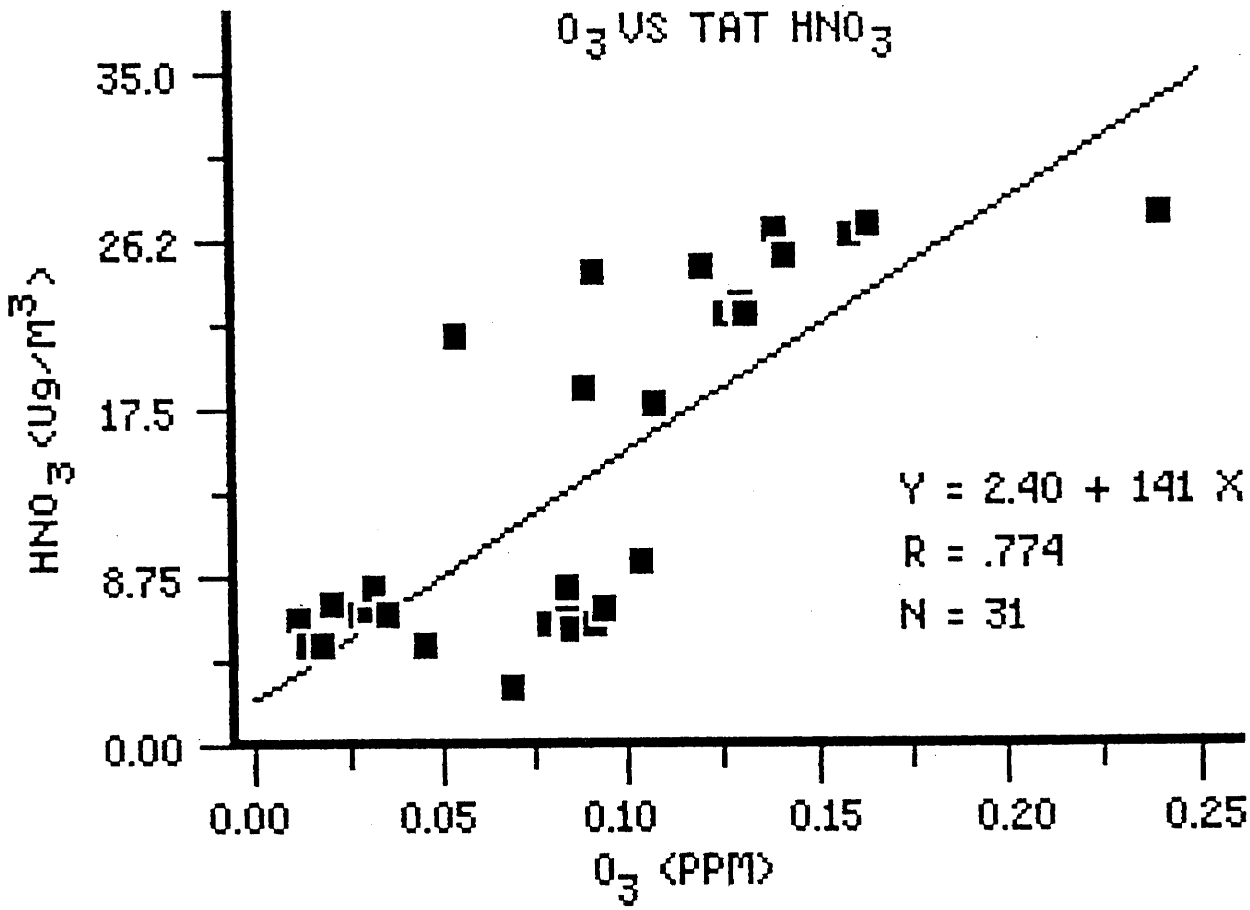

O3 VS TAT HNO3
35.0
26.2
17.5
8.75
0.00
HNO3 <Ug/M3>
0.00
0.05
0.10
0.15
0.20
0.25
O3 <PPM>
Y = 2.40 + 141 X
R = .774
N = 31

Figure 14

TABLE 24

Comparison of DDM and Tunable Diode Laser (TDL) HNO_3 Results ($\mu g/m^3$)

Date	Period[a]	DDM	TDL[b]	Date	Period[a]	DDM	TDL[b]
9/11/85	2	1.0	0.46	9/15/85	1	3.0	1.62
	3	5.3	2.2		2	16.1	8.53
	4	3.4	1.97		3	18.3	15.9
	5	1.2	0.97		4	9.6	11.6
					5	0.7	4.4
9/12/85	1	1.0	0.4	9/16/85	1	1.0	3.47
	2	7.0	4.50		2	5.9	2.39
	3	8.6	6.16		3	9.1	2.56
	4	22.6	18.6		4	5.5	--
	5	8.2	6.96		5	1.6	1.92
9/13/85	1	3.4	3.61	9/17/85	1	1.9	5.93
	2	--	3.83		2	6.1	2.86
	3	27.2	15.6		3	10.1	8.11
	4	30.8	17.0		4	5.5	8.00
	5	10.2	9.7		5	0.8	5.43
9/14/85	1	7.0	5.36	9/18/85	1	0.6	5.55
	2	25.3	12.9		2	0.7	2.96
	3	47.4	32.2		3	1.9	6.2
	4	31.2	30.5		4	1.2	3.73
	5	6.5	3.53		5	0.3	2.71
				9/19/85	1	0.3	0.70

a. Period 1 00-06 hours
Period 2 08-12 hours
Period 3 12-16 hours
Period 4 16-20 hours
Period 5 20-24 hours

b. Calculated from data supplied by G. Mackay, Unisearch, Inc.

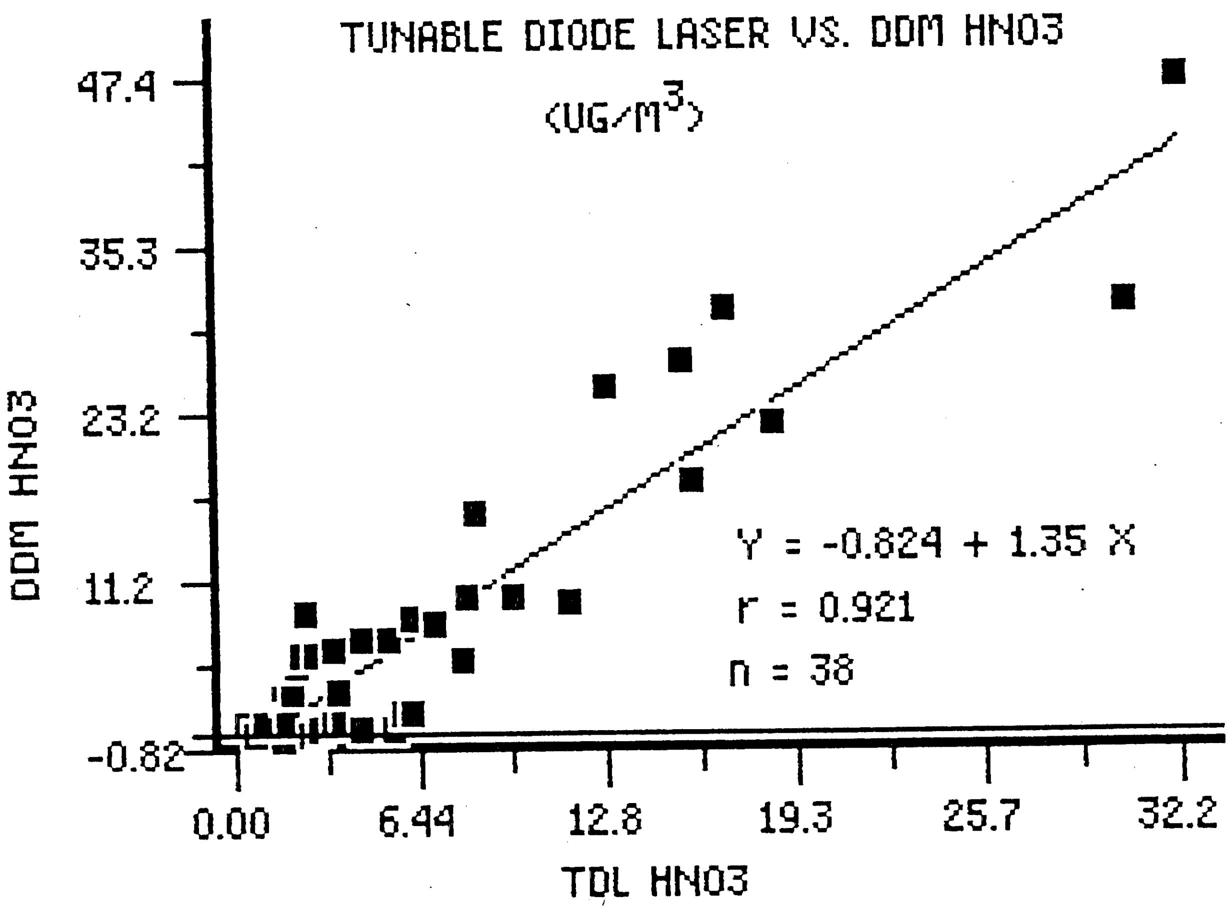

TUNABLE DIODE LASER VS. DDM HNO3
(UG/M3)
47.4
35.3
23.2
11.2
-0.82
DDM HNO3
0.00
6.44
12.8
19.3
25.7
32.2
TDL HNO3
Y = -0.824 + 1.35 X
r = 0.921
n = 38

Figure 15

TABLE 25

COMPARISON OF TUNGSTIC ACID TECHNIQUE AND

FILTER PACK FOR AMMONIA (Ug/M³ AS NH_4+)

DATE	PERIOD (PDT)	TAT[A]	FILTER PACK
09/14/85	0800-1200	1.7[B]	4.6
09/14/85	1200-1600	1.9	5.4
09/14/85	1600-2000	2.5	4.5
09/14/85	2000-2400	3.8	3.5
09/15/85	0000-0600	4.4	2.8
09/15/85	0800-1200	2.9[C]	6.7
09/15/85	1200-1600	2.6	7.8
09/15/85	1600-2000	2.8	3.7
09/15/85	2000-2400	5.2	4.0
09/16/85	0000-0600	4.9	2.3
09/16/85	0800-1200	11.5[B]	17.3
09/16/85	1200-1600	6.0	7.2
09/16/85	1600-2000	2.5	2.7
09/16/85	2000-2400	3.0	2.0
09/17/85	0000-0600	2.8[D]	3.0
09/17/85	0800-1200	14.3	---[E]
09/17/85	1200-1600	8.4	7.2
09/17/85	1600-2000	4.1	2.7
09/17/85	2000-2400	3.1	2.6
09/18/85	0000-0600	3.1	2.0
09/18/85	0800-1200	3.4	2.1
09/18/85	1200-1600	2.5	1.3
09/18/85	1600-2000	1.5[B]	1.8
09/18/85	2000-2400	3.2	2.6
09/19/85	0000-0600	2.3	1.1

[A] Mean of four or six 1-hr values, except as noted
[B] Mean of two, 1-hr values
[C] Mean of three, 1-hr values
[D] Mean of five 1-hr periods
[E] Sample rejected

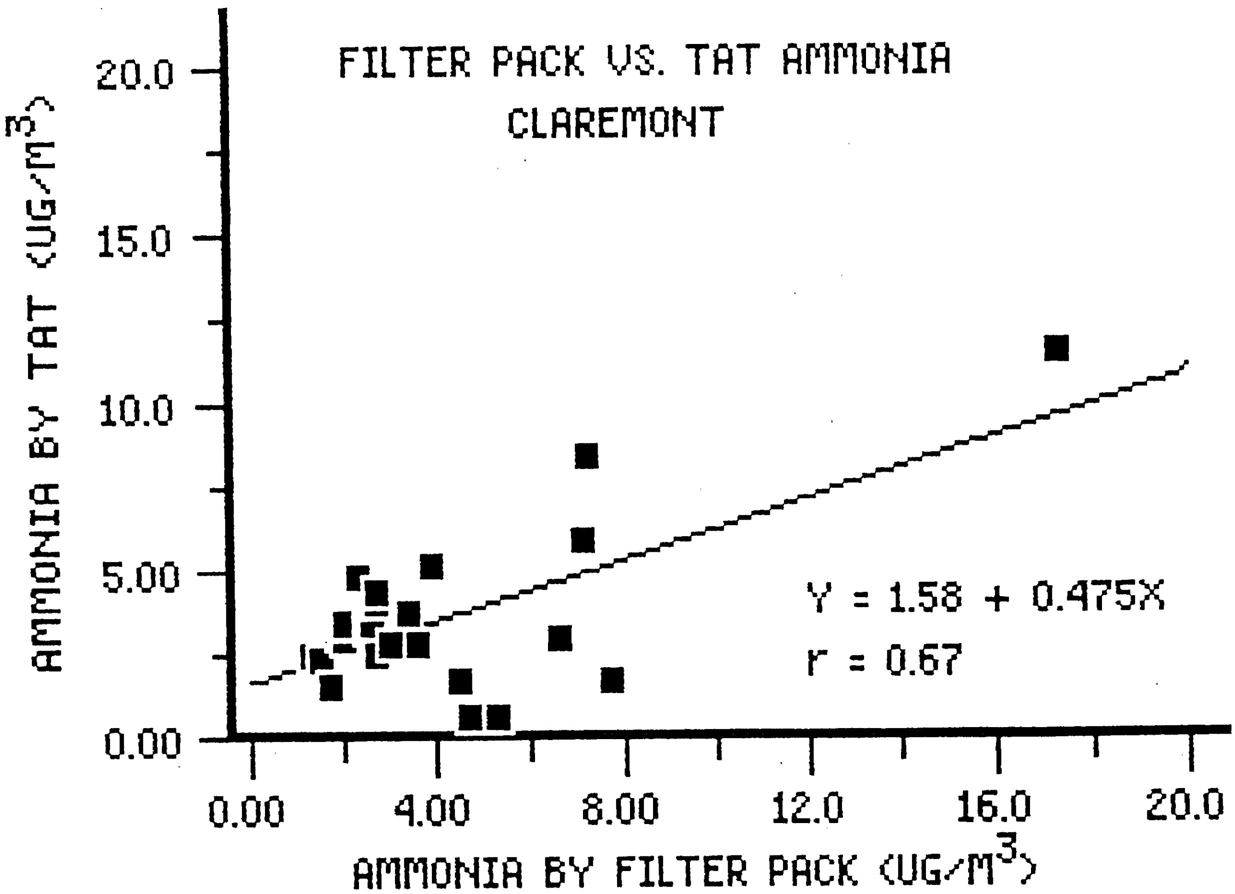
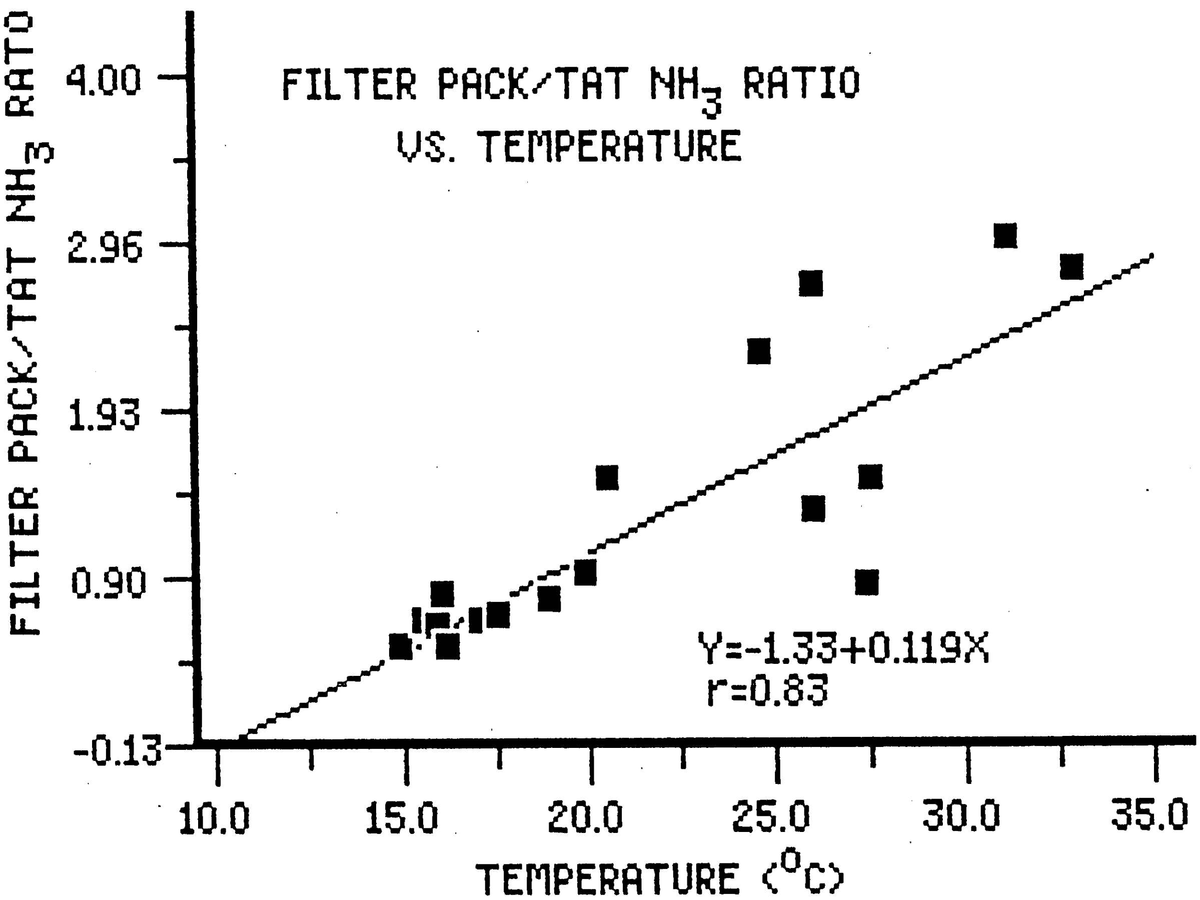

FILTER PACK VS. TAT AMMONIA
CLAREMONT
AMMONIA BY TAT (UG/M3)
20.0
15.0
10.0
5.00
0.00
0.00
4.00
8.00
12.0
16.0
20.0
AMMONIA BY FILTER PACK (UG/M3)
Y = 1.58 + 0.475X
r = 0.67

Figure 16



FILTER PACK/TAT NH3 RATIO
VS. TEMPERATURE
FILTER PACK/TAT NH3 RATIO
4.00
2.96
1.93
0.90
-0.13
10.0
15.0
20.0
25.0
30.0
35.0
TEMPERATURE (°C)
Y=-1.33+0.119X
r=0.83

Figure 17

TABLE 26

AMMONIA METHOD COMPARISON (TAT V.S. FP)

BY TIME OF DAY (Ug NH3/M3 AS NH4+)

TIME PERIOD (PDT)	DATE	FP/TAT	MEAN RATIO
0000-0600	9/15/85	0.64	
	9/16	0.47	
	9/17	1.07	0.66 ± 0.24
	9/18	0.65	
	9/19	0.48	
0800-1200	9/14	2.71	
	9/15	2.31	1.79 ± 0.93
	9/16	1.50	
	9/18	0.62	
1200-1600	9/14	2.84	
	9/15	3.0	
	9/16	1.2	1.68 ± 1.15
	9/17	0.86	
	9/18	0.52	
1600-2000	9/14	1.80	
	9/15	1.32	
	9/16	1.08	1.21 ± 0.41
	9/17	0.66	
	9/18	1.20	
2000-2400	9/14	0.92	
	9/15	0.77	
	9/16	0.67	0.80 ± 0.09
	9/17	0.84	
	9/18/85	0.80	

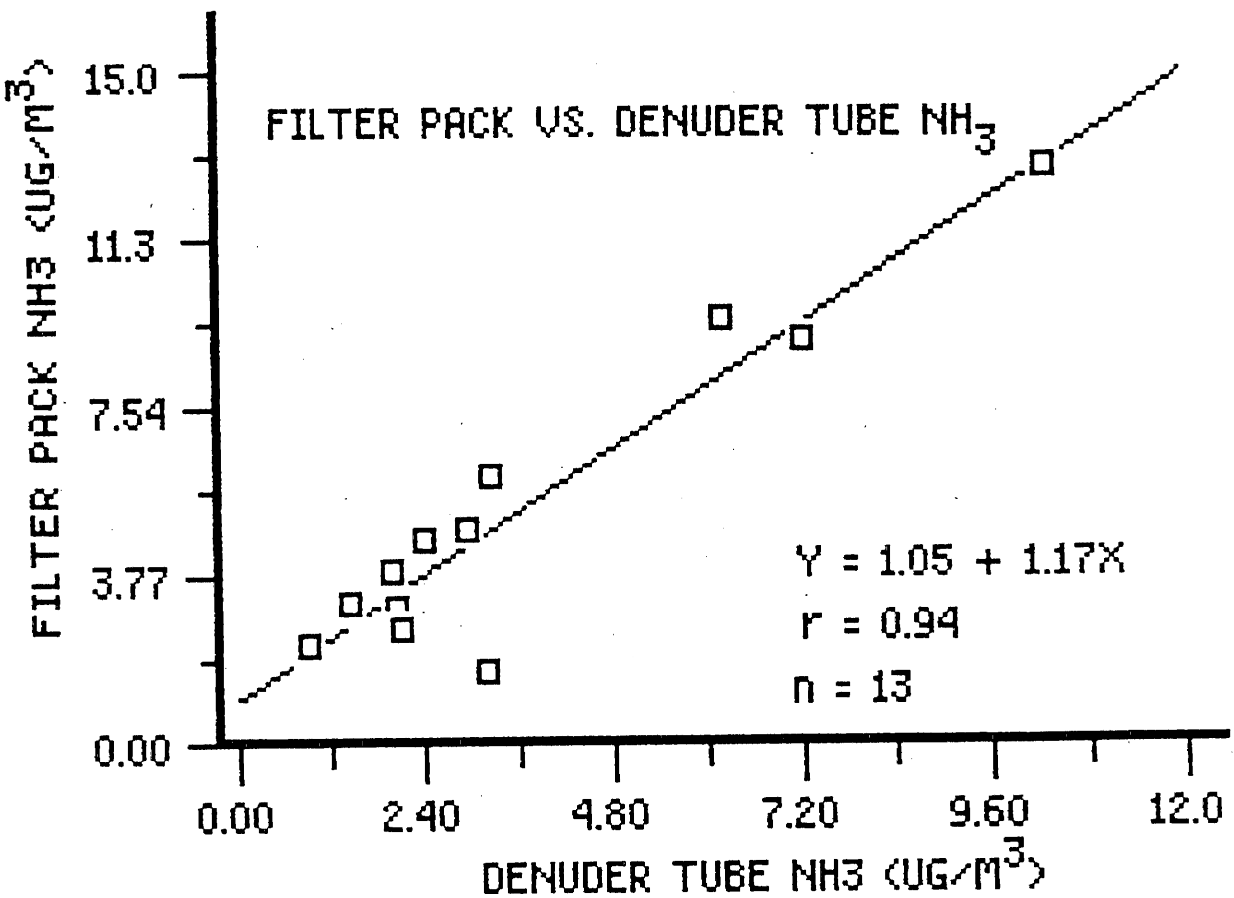
TABLE 27

COMPARISON OF FILTER PACK AND OXALIC ACID DENUDER TUBE

COLLECTION OF GASEOUS AMMONIA (Ug/M3 AS NH4+)

STARTING DATE	PERIOD (PDT)	FILTER PACK	DENUDER TUBE
09/11/85	0800-2000	3.1	2.0
09/11/85	2000-0600	3.2	1.4
09/12/85	0800-2000	13.0	10.3
09/12/85	2000-0600	4.6	2.4
09/13/85	0800-2000	9.6	6.2
09/13/85	2000-0600	3.9	2.0
09/14/85	0800-2000	4.8	3.0
09/14/85	2000-0600	3.1	1.4
09/15/85	0800-2000	6.0	3.3
09/15/85	2000-0600	---[a]	---[a]
09/16/85	0800-2000	9.1	7.2
09/16/85	2000-0600	2.6	2.1
09/17/85	0800-2000	---[a]	8.3
09/17/85	2000-0600	2.2	0.9
09/18/85	0800-2000	1.7	---[a]
09/18/85	2000-0600	1.7	3.2

[a] No data.



FILTER PACK VS. DENUDER TUBE NH3
Y = 1.05 + 1.17X
r = 0.94
n = 13
15.0
11.3
7.54
3.77
0.00
FILTER PACK NH3 (UG/M3)
0.00
2.40
4.80
7.20
9.60
12.0
DENUDER TUBE NH3 (UG/M3)

Figure 18

To assess the source of temperature sensitivity in the FP/TAT NH_3 ratio, Figures 19 and 20 plot ratios of NH_3 results, FP/DT and TAT/DT, respectively, against T. Assuming the DT to be relatively insensitive to temperature change, the TAT exhibits a much greater temperature sensitivity than does the FP. Based on Figures 15 to 18, the TAT NH_3 results appear to be subject to both positive and negative errors of about a factor of 2.

C. Particulate NH_4^+ vs. Gaseous NH_3

Tables 16 and 17 tabulated the FP results for apparent particulate NH_4^+ and gaseous NH_3. The ratio of mean values, particulate/gaseous NH_3 as measured with the FP is 0.46. However, based on comparison with the DT method, the NH_3 results averaged 50% too high. The particulate NH_4^+ results should be correspondingly too low. The corrected mean ratio particulate/gaseous NH_3 is inferred to be about 2.

D. Ammonium Nitrate Dissociation as a Source of HNO_3 and NH_3

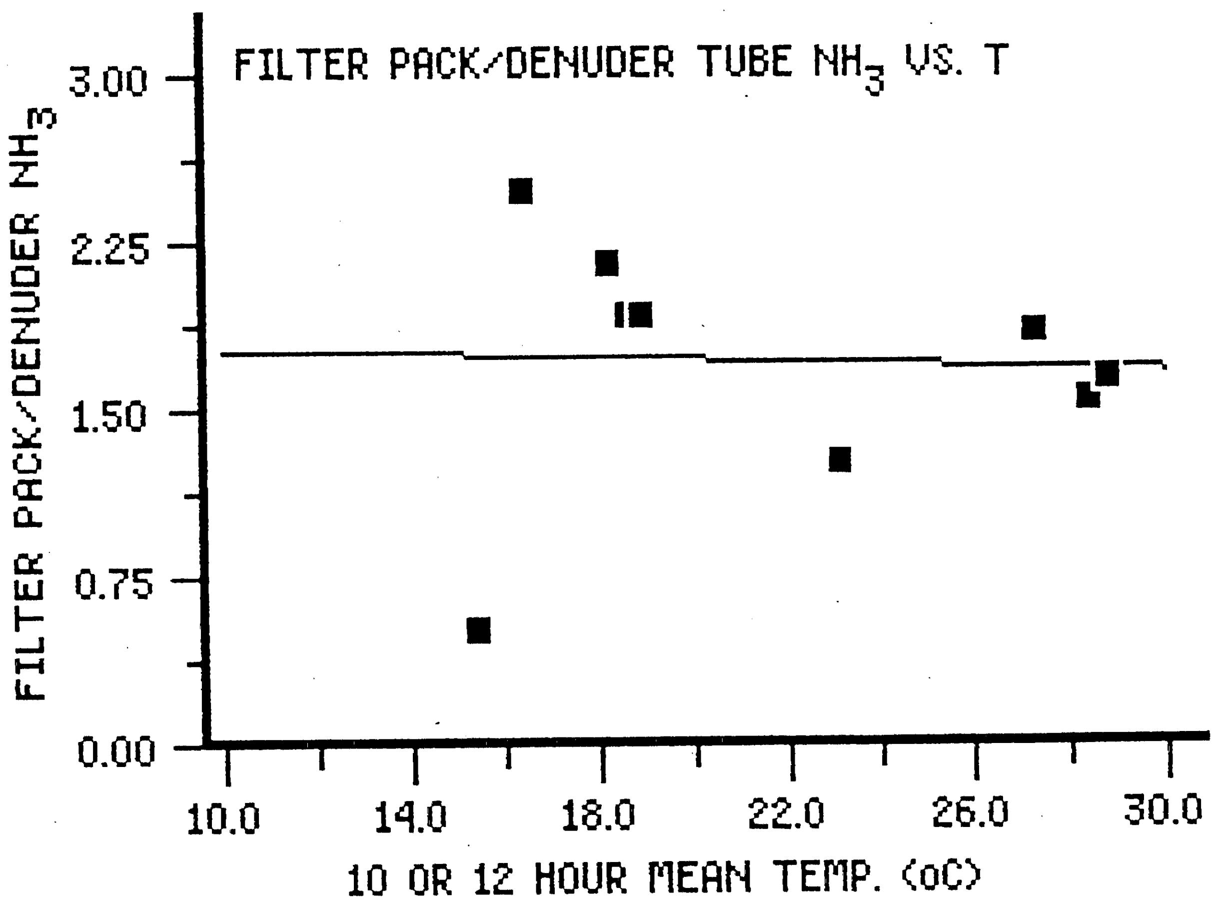
In the absence of local sources of HNO_3 or NH_3, the atmospheric concentrations of these species might be controlled by the equilibrium:

$$NH_4NO_3 \rightleftarrows NH_3\ (g) + HNO_3\ (g)$$
$$K_d = (NH_3)(HNO_3)$$

The concentration product $(NH_3)(HNO_3)$ was calculated for four or six hour average periods employing DDM HNO_3 results and corrected NH_3 values. The latter were obtained as the expected DT concentration using FP results and the regression equation (Figure 17):

$$FP = 1.05 + 1.17\ DT$$

The results, together with corresponding mean temperatures, are given in Table 28. The dissociation constant is plotted against inverse temperature in Figure 21. Data are segregated between those above and below the approximate deliquescence R.H., 60%. The solid line shows the theoretical temperature dependence of solid NH_4NO_3 derived by Stelson and Seinfeld (18):



FILTER PACK/DENUDER TUBE NH_3 VS. T
FILTER PACK/DENUDER NH_3
3.00
2.25
1.50
0.75
0.00
10.0
14.0
18.0
22.0
26.0
30.0
10 OR 12 HOUR MEAN TEMP. (oC)

Figure 19

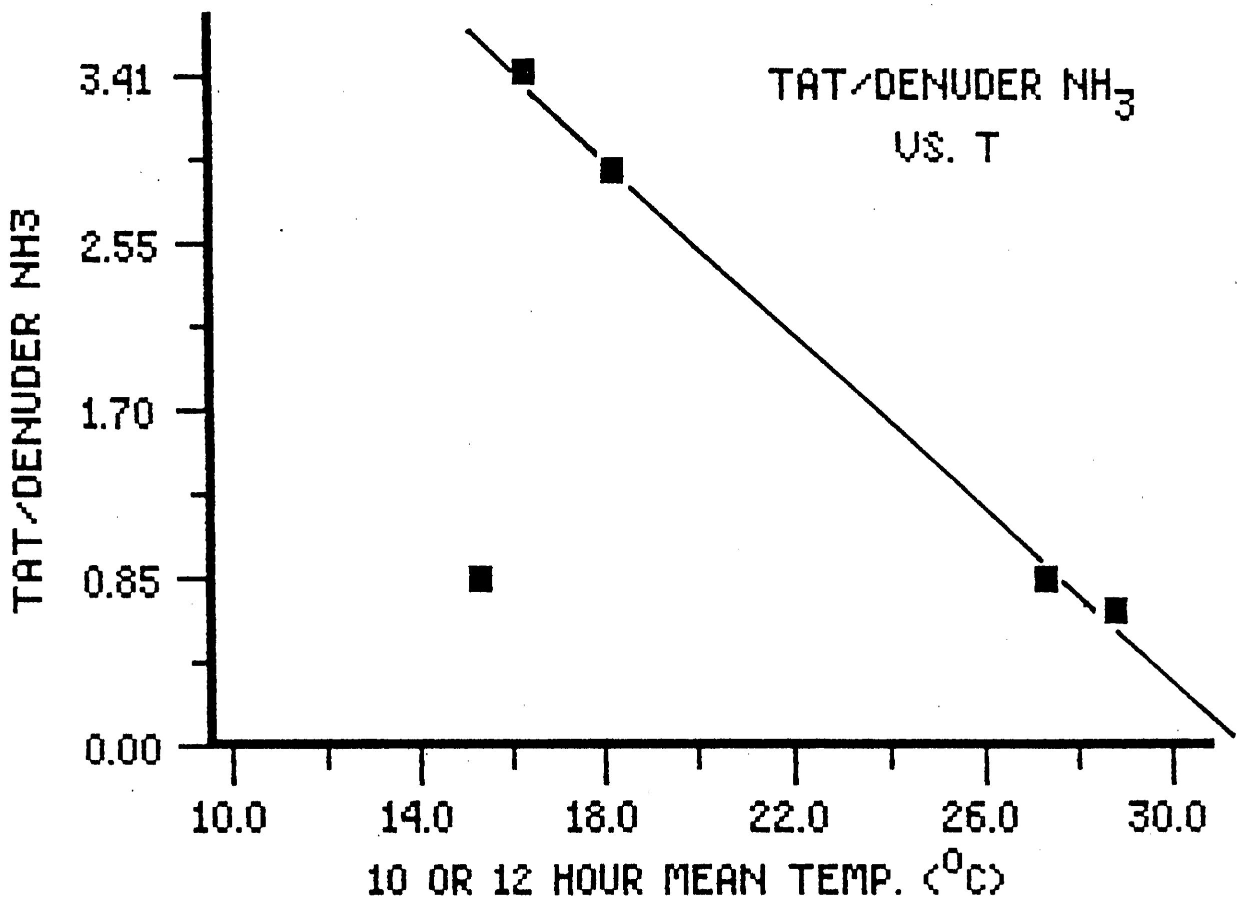

TAT/DENUDER NH3
VS. T
TAT/DENUDER NH3
3.41
2.55
1.70
0.85
0.00
10.0
14.0
18.0
22.0
26.0
30.0
10 OR 12 HOUR MEAN TEMP. (°C)

Figure 20

TABLE 28

CALCULATED AMMONIUM NITRATE DISSOCIATION CONSTANT

DATE	PERIOD (PDT)	$(NH_3)*(HNO_3)$[A] $(PPB)^2$	MEAN TEMP (°C)
09/11/85	0800-1200	0.75	----[B]
09/11/85	1200-1600	5.58	----[B]
09/11/85	1600-2000	3.25	----[B]
09/11/85	2000-2400	1.18	23.8
09/12/85	0000-0600	0.99	24.2
09/12/85	0800-1200	14.48	19.5
09/12/85	1200-1600	97.45	23.3
09/12/85	1600-2000	68.05	26.4
09/12/85	2000-2400	15.79	20.6
09/13/85	0000-0600	4.99	17.7
09/13/85	0800-1200	----[B]	25.2
09/13/85	1200-1600	105.40	31.0
09/13/85	1600-2000	84.39	29.0
09/13/85	2000-2400	15.24	20.5
09/14/85	0000-0600	8.04	17.3
09/14/85	0800-1200	41.17	26.0
09/14/85	1200-1600	94.57	32.9
09/14/85	1600-2000	50.06	24.8
09/14/85	2000-2400	7.29	19.9
09/15/85	0000-0600	2.39	17.0
09/15/85	0800-1200	41.45	24.7
09/15/85	1200-1600	56.45	31.2
09/15/85	1600-2000	11.56	26.1
09/15/85	2000-2400	0.94	18.9
09/16/85	0000-0600	0.58	16.2
09/16/85	0800-1200	44.07	20.5
09/16/85	1200-1600	25.64	27.6C
09/16/85	1600-2000	4.27	----[B]
09/16/85	2000-2400	0.71	----[B]
09/17/85	0000-0600	1.71	----[B]
09/17/85	0800-1200	----[B]	24.6[D]
09/17/85	1200-1600	28.69	27.4
09/17/85	1600-2000	4.17	27.1[C]
09/17/85	2000-2400	0.57	17.6
09/18/85	0000-0600	0.26	15.6
09/18/85	0800-1200	0.33	15.9
09/18/85	1200-1600	0.23	17.6
09/18/85	1600-2000	0.40	18.1
09/18/85	2000-2400	0.21	16.1
09/19/85	0000-0600	0.00	14.9

[A] HNO_3 values are from the DDM. NH_3 resultes are based on FP values corrected to the equivalent denuder tube value with the equation : FP= 1.05 +1.17 DT.

[B] Insufficient data.

[C] Average of one hour only.

[D] Average of three hours.

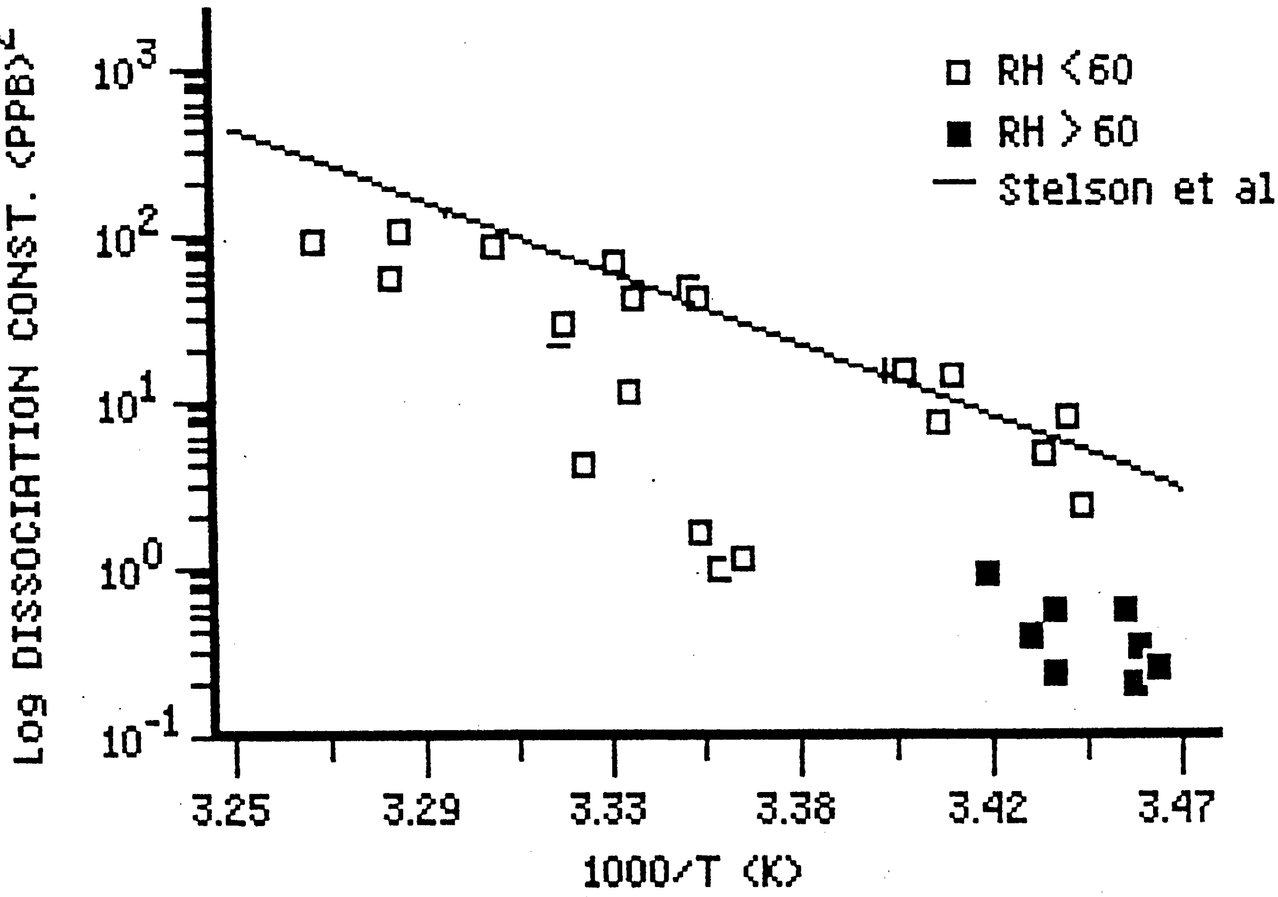


Figure 21

Dissociation Constant for NH_4NO_3 vs. Inverse Temperature

$$\ln K = 84.6 - \frac{24420}{T} - 6.1 \ln\left(\frac{T}{298}\right)$$

The line appears to provide an upper limit to the experimental results at < 60% R.H. Figure 21 excludes results for the periods 1200-1600, 9/12/85 and 0800-1200, 9/16/85, when the very high NH_3 results suggest the sampling of NH_3 from a local source (e.g. animal feed lots).

E. Conclusions

1. The denuder difference method yielded results about 30% higher than those by the tunable diode laser (TDL). However, probable HNO_3 loss in the inlet of the TDL units suggests the DDM to be accurate within about 20%.*

2. In comparison to the DDM, the tungstic acid technique (TAT) is subject to positive error in HNO_3 measurement. TAT HNO_3 range from about equal during daylight hours to a factor of 6 higher than the DDM at night (or during periods of lower temperature and higher R.H.)

3. The cause of the higher TAT HNO_3 results is unknown. However the retention on the TAT preconcentrator of nitrogen-containing pollutants (other than HNO_3) is likely. Nitrous acid, N_2O_5, and NO_3 may contribute to such differences.

4. Ammonia results with the TAT can be too large or too small by about a factor of two. High temperatures (and/or low humidities) favor negative errors for NH_3 with the TAT.

5. Ammonia results with the filter pack method averaged about 50% too high.

*This conclusion is further strengthened by a comparison of the TDL and 1-hour average Fourier transform infra-red results (19) indicating the TDL values to average about 15% lower than those by FTIR.

REFERENCES

1. B.R. Appel, Y. Tokiwa and M. Haik. Sampling of Nitrates in Ambient Air. Atmos. Environ. 15, 283-289 (1980).

2. B.R. Appel, Y. Tokiwa, V. Povard, E.L. Kothny and J.J. Wesolowski. Determination of Acidity in Ambient Air. Final Report to the California Air Resources Board, Contract No. A1-159-32 (1984).

3. C.W. Spicer, J.E. Howes, Jr., T.A. Bishop and L.H. Arnold. Nitric Acid Measurement Methods: An Intercomparison. Atmos. Environ. 16, 1487-1500 (1982).

4. R.S. Braman, T.J. Shelly and W.A. McClenny. Tungstic Acid for Preconcentration and Determination of Gaseous and Particulate Ammonia and Nitric Acid in Ambient Air. Anal. Chem. 54, 358-364 (1982).

5. W.A. McClenny, K. Kaneda, T. Yanaka and R. Sugai. Tungstic Acid Technique for Monitoring Nitric Acid and Ammonia in Ambient Air. Anal. Chem. 54, 365-369 (1982).

6. P.C. Gailey, W.A. McClenny, R.S. Braman, and T.J. Shelley. A Simple Design for Automation of the Tungsten VI Oxide Technique for Measurement of NH_3 and HNO_3. Atmos. Environ. 17, 1517-1519 (1983).

7. W. John and G. Reischl. Measurements of the filtration efficiencies of selected filter types. Atmos. Environ. 12, 2015-2019 (1978).

8. B.R. Appel, S.M. Wall, Y. Tokiwa and M. Haik. Simultaneous Nitric Acid, Particulate Nitrate and Acidity Measurements in Ambient Air. Atmos. Environ. 14, 549-554. (1980).

9. W.F. Koch. Complication in the Determination of Nitrite by Ion Chromatography. Anal. Chem. 51, 1571 (1979).

10. K.G. Anlauf, P. Fellin, H.A. Weibe, H.I. Schiff, G.I. Mackay, R.S. Braman and R. Gilbert. "A Comparison of Three Methods for Measurement of Atmospheric Nitric Acid and Aerosol Nitrate and Ammonium," Atmos. Environ. 19, 325-333 (1985).

11. S.M. Japar and W.W. Brachaczek. Artifact sulfate formation from SO_2 on nylon filters. Atmos. Environ. 18, 2479-2482 (1984).

12. E. Sanhueza, C.N. Plum and J.N. Pitts, Jr. Positive Interference of Nitrous Acid in the Determination of Gaseous HNO_3 by the NO_x chemiluminescence-Nylon cartridge Method: Applications to the Measurements of PPB Levels of HONO in Air. Atmos. Environ. 18, 1029-1031 (1984).

13. B.R. Appel, V. Povard and J.J. Wesolowski. Final Report. Sampling and Analytical Problems in Air Pollution Monitoring Phase II, Year 2, EPA Cooperative Agreement No. CR810798-02-0 (1985).

14. B.R. Appel, Y. Tokiwa, J. Hsu, E.L. Kothny and E. Hahn. Visibility as Related to Atmospheric Aerosol Constituents. Atmos. Environ. 19, 1525-1534 (1985).

15. B.R. Appel, Y. Tokiwa, M. Haik and E.L. Kothny. Artifact Particulate Sulfate and Nitrate Formation on Filter Media. Atmos. Envion. 18, 409-416 (1984).

16. W. John, Private Communication (1986).

17. G. Mackay, Private Communication (1986).

18. A.W. Stelson and J.H. Seinfeld. Relative Humidity and Temperature Dependence of the Ammonium Nitrate Dissociation Constant. Atmos. Environ. 16:983-992 (1982).

19. D. Lawson. Nitrogen Species Method Comparison Studies at Claremont, California, September 1985 - Overview. Presented at the 1986 EPA/APCA Symposium on Measurement of Toxic Air Pollutants, April, 1986.